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Evaluation of Tubewall Corrosion Rates on a Coal-Fired Utility Boiler Using Staged Combustion for NOx Reduction

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EVALUATION OF TUBEWALL CORROSION RATES ON A COAL-FIRED UTILITY BOILER USING STAGED COMBUSTION FOR NO_x REDUCTION

by

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16. ABSTRACT
The report discusses NOx emissions, at an existing coal-firing utility boiler, that have been controlled by modifying normal combustion parameters using the boiler's normal operating control system (without adding new hardware). The combustion modifications (CMs) studied included unusual fuel/air ratios at selected burner elevations (staged combustion) and decreased excess air flow rates. Side effects of the new operating conditions were also studied, including: changes in boiler efficiency, other emissions, and (for the first time) detailed studies of boiler tubewall corrosion rates. Wall thickness measurements revealed that, averaged over the total measured area, the boiler walls lost 2.2 mils (5.2 mils/yr) during the 5-month baseline period: 2.6 mils (6/2 mils/yr) in the non-burner zones, compared to 1.7 mils (4.0 mils/yr) in the burner zone. During the 12-month low-NOx period, the non-burner elevations lost only 2.11 mils/yr, while the burner area lost 5.05 mils/yr. This corrosion rate in the burner zone for the low-NOx period is statistically significantly higher than that for the same zone during the baseline period. Generally, no radical side effects were detected after NOx emissions were decreased by as much as 50%. Typically, at full load, NOx reductions of more than 20% were easily achieved by combustion modifications.

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ABSTRACT

NO_x emissions at a coal-fired utility boiler have been decreased through modification of existing combustion parameters using the boiler's existing hardware. The combustion modifications (CM) studied included decreased excess air flow rate, and a variety of fuel/air ratios at selected burner elevations (biased combustion). Side effects of these operating conditions were also studied, including: changes in boiler efficiency (but not heat rate), other emissions, and, for the first time, detailed studies of boiler wall corrosion rate. Wall thickness measurements revealed that averaged over the total measured area, the boiler walls lost 2.2 mils (5.2 mils/yr) during the 5 month "baseline" period: 2.6 mils (6.2 mils/yr) in the nonburner zones compared to 1.7 mils (4.0 mils/yr) in the burner zone. During the 12 month "Low-NO_x" period, the non-burner elevations lost only 2.11 mils/yr, while the burner area lost 5.05 mils/yr; a slightly higher loss rate in the burner zone than for the same zone during the baseline period. Generally, no significant side effects were detected after NO_x emissions were decreased by as much as 50% at decreased load. Typically, near full load, NO_x reductions of about 20% were achieved through combustion modifications such as biased burner firing and decreased boiler excess air. Therefore, the corrosion rates experienced during extended "Low-NO_x" operation would not appear to appreciably reduce the expected life of the furnace tubes.

DISCLAIMER

Although every reasonable effort has been made to assure the accuracy and quality of the data presented herein, it is intended to be used as only one of many tools available to the reader. Engineering or other decisions should not be based solely upon the contents of this report. Rather, this report should be used in conjunction with the many other relevant publications available.

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h5358

TABLE OF CONTENTS

Page

DISCLAIMER ii

ABSTRACT ii

ACKNOWLEDGEMENT xii

SUMMARY 1

1. INTRODUCTION 5

2. FIELD STUDY PLANNING PROCEDURES 8

  2.1 Selection and Description of Test Boiler (Crist No. 7) 8

  2.2 Test Program Strategy 10

  2.3 Corrosion Measurements on Fireside of Furnace's Water Walls 10

    2.3.1 Corrosion Probes 12

    2.3.2 Ultrasonic Furnace Tube Wall Thickness Measurements 16

    2.3.3 Tube Wall Test Panels 18

  2.4 Gaseous Sampling and Analysis System 22

    2.4.1 Flue Gas at Economizer Outlet 22

    2.4.2 Gaseous Sample at Furnace Wall 29

  2.5 Particulate Sampling: Mass - Size Distribution 30

  2.6 Boiler Efficiency 31

  2.7 SO_2/SO_3 Gaseous Sampling 32

  2.8 SASS Train Sampling of Stack Emissions 33

    2.8.1 Analytical Methodology 33

    2.8.2 Sampling and Analysis 34

3. RESULTS AND DISCUSSIONS 36

  3.1 Gaseous Emission Results (NO_x, CO, HC, SO_2) and Investigated NO_x Control Methods ... 36

k5358

TABLE OF CONTENTS (CONT'D)

Page

3.1.1 Effect of Secondary Air Register Settings on NO_x Emissions 43

3.1.2 Effect of Firing Pattern on NO_x Emissions 46

3.1.3 Effect of Load on NO_x Emissions 48

3.1.4 Effect of Excess Air on NO_x Emissions 48

3.1.5 Effect of Partial Staging on NO_x Emissions 57

3.1.6 Optimum CM for NO_x Control 57

3.2 Furnace Waterwall Fireside Corrosion Results 61

3.2.1 Corrosion Probes 61

3.2.2 Ultrasonic Measurements of Furnace Tubes 72

3.2.3 Tube Wall Corrosion Test Panels 109

3.2.4 Correlation of Test Panel, Furnace Tube and Probe Coupon Corrosion Data 117

3.3 Relationship Between Furnace Gas Measurements and Corrosion Results 122

3.3.1 Furnace Gas Tap Results 122

3.3.2 Tube Wall Corrosion Measurements 129

3.3.3 Correlation Between Furnace Gas, and Wall Thickness Measurements 129

3.4 Particulate Emission Results (Precipitator Inlet) 137

3.5 Boiler Efficiency Results 140

3.6 SO_2/SO_3 Gaseous Sampling Results 140

3.7 SASS Tests - Results and Discussion 144

3.7.1 Metals in Coal 144

3.7.2 Metals 145

3.7.3 Mass Spectrometry Analysis 145

h5358

TABLE OF CONTENTS (CONT'D)

Page

4. CONCLUSION AND RECOMMENDATIONS 161

    4.1 Gaseous Emissions Measurements 161

    4.2 Conclusions and Recommendations on Corrosion Measurements 162

REFERENCES 166

APPENDIX A - Program Schedule 169

APPENDIX B - Summary of Flue Gas Compositions 170

APPENDIX C - Sample Data Tables (Both Raw and Reduced) 173

APPENDIX D - Conversion Factors 178

APPENDIX E - Analytical Procedures for SASS Train Samples 180

APPENDIX F - Results of SASS Infra-Red (IR) Analysis 217

APPENDIX G - Ultrasonic Thickness Gauge, Users Manual (Selected Pages) 237

APPENDIX H - Foster Wheeler Evaluation of Tubewall Corrosion 241

LIST OF FIGURES

Number	Title	Page
2-1	Cross Section of CRIST, Unit 7 Boiler	11
2-2	Boiler Layout	13
2-3	Corrosion Probe	14
2-4	Corrosion probe (cross sectional view)	15
2-4.1	Event Chart: Panel exposure & wall thickness measurements	19
2-4.2	Corrosion Test Panel Installation and Measurement Schedule	20
2-5	General Layout and Flue Gas Sampling Points	23
2-6	Gaseous Sampling System	24
2-7	Exxon Research Transportable Sampling and Analytical System	25
2-8	Schematic of Source Assessment Sampling System (SASS)	35
3-1	NO_x vs. Firing Mode (For Damper Configuration "D")	49
3-2	NO_x vs. Load	51
3-3	NO_x vs. O_2 for Various Air Register Settings	54
3-4	NO_x vs. O_2, and CO vs. O_2	56
3-5	Staged Combustion: NO_x vs. Degree of Staging	58
3-6	Comparison of Corrosion Rates	71
3-7	Shewart Control Charts	91
3-8	Baseline Half - Wall Average Thickness Change Low NO_x Half - Wall Average Thickness Change	93
3-9	95% Simultaneous Confidence Limits - Crist No. 7 Furnace Half and Full Walls (5 Month Baseline Operation)	100
3-10	95% Simultaneous Confidence Limits - Crist No. 7 Furnace Half and Full Walls (12 Month Low NO_x Operation)	103

LIST OF FIGURES (CONT'D)

Number	Title	Page
3-11	Comparison of 5 Month Baseline and 12 Month Low NO_x Corrosion Data	107
3-12	Test Panel Measurements by Metal Type - 5 Tubes per Panel (Average Change in Tube Hot Side Wall Thickness - Mils)	112
3-13	Test Panel Measurements and Locations (Average Change in Tube Wall Thickness - Mils)	114
3-14	CO vs. O_2 (for Gas Taps 1-7)	126
3-15	CO vs. O_2 (for Gas Taps 8-11)	127
3-16	CO vs. O_2 (for Gas Taps 12-14, 16, 18, and 19)	128
3-17	Corrosion Rate vs. CO in the Furnace for the Top Burner Elevation	136
3-18	Particulate Size Distribution	141
E-1	Sample Analysis Procedures for SASS Cyclones, and Organic Module Samples	181

Note: Most of the figures in the Appendixes are not numbered, and as such, are not listed here.

e5358

LIST OF TABLES

Number	Title	Page
2-1	Test Panel Locations	18
2-2	Mobile Analytical Laboratory: Continuous Gas Monitors and Calibration Standards	27
2-3	Composition of Standard Gas Mixtures Used for Calibration of Gas Analyzers (for use with Table 2-2)	28
3-1	Flue Gas Tests - (Tests Numbers Grouped by Test Conditions)	37
3-2	Test and Date Cross Reference Table - Part I by test number, Part 2 by date (Test Numbers & Dates Performed)	40-41
3-3	History of Secondary-Air-Damper Settings (Percent Open)	44
3-4	Secondary Air Damper Configurations	45
3-5	Secondary Air Distribution vs. Secondary Air Damper Configuration	45
3-6	Firing Pattern Nomenclature	47
3-7	Key to Figure 3-1 (NO_x vs. Firing Mode)	50
3-8	Key to Figure 3-2: NO_x vs. Load	52
3-9	Key to Figures 3-3 and 3-4 NO_x and/or CO vs. Excess Air	55
3-9.1	Low-NO_x Guidelines	60
3-10	24 Hour, Low-NO_x Corrosion Rate Data (By Probes)	62
3-11	25 Hour, Baseline Corrosion Rate Data (By Probes)	63
3-12	30 Hour, Baseline Corrosion Rate Data (By Probes)	64
3-13	180 to 260 Hour Low-NO_x Corrosion Rate Data (By Probes).	65
3-14	290 Hour Baseline Corrosion Rate Data (By Probes)	66
3-15	290 Hour Baseline and Low-NO_x Corrosion Rate Data (By Probes)	67
3-16	597 and 738 Hour Low-NO_x Corrosion Rate Data (By Probes)	68

LIST OF TABLES (CONT'D)

Number	Title	Page
3-17	1000 Hour Baseline Corrosion Rate Data (By Probes)	69
3-18	Frequency Tallies of Measurement Errors	74
3-19	Tubewall Thickness Measurements - Mils	75
3-20	Statistical Analysis of Possible Bias Caused by Sandblasting Tubes (Baseline Operation Period 5/76 to 10/76)	76
3-21	Statistical Analysis of Possible Bias Caused by Sandblasting Tubes (Baseline Operation Period 5/76 to 10/76 - Screened Data)	78
3-22	Tubewall Thickness Measurements - Mils	79
3-23	Statistical Analysis of Sandblast Measurements vs. Non-Sandblast Measurements (Left Sidewall Measurements)	81
3-24	Statistical Analysis of Possible Bias Caused by Sandblasting Tubes (Right Sidewall Measurements)	82
3-25	Statistical Analysis of Possible Bias Caused by Sandblasting Tubes (Left Sidewall Measurements)	85
3-26	Statistical Analysis of Possible Bias Caused by Sandblasting Tubes (Right Sidewall Measurements)	86
3-27	Tubewall Hot Side Metal Thickness Changes - Mils	89
3-28	Tubewall Hot Side Metal Thickness Change Rate - Mils/Year	90
3-29	Correlation of Baseline vs. Low NO_x Half-Wall Averages	92
3-30	Detailed Calculations for Left Sidewall - Baseline Operation	95
3-31	Alternate Estimates of Overall Variance of Measurement (of Level Means) for Walls of Crist No. 7 Furnace	96
3-32	Values of Equivalent Degrees of Freedom for Mean Square Successive Differences of Orders 1 to 3 Based on 3 to 6 Successive Values	97

f5358

LIST OF TABLES (CONT'D)

Number	Title	Page
3-33	Individual and Simultaneous 95% Confidence Limits	98
3-34	Alternate Estimate of Overall Variance of Measurements (or Level Means) for Walls of Crist No. 7 Furnace, Low NO_x Operation	101
3-35	Individual and Simultaneous 95% Confidence Limits (Low NO_x Operation - Mils or Mils Per Year)	102
3-36	Comparison of 5-Month Baseline and 12-Month Low NO_x Average Tube Wall Thickness Loss Data	105
3-37	Projected Tube Wall Thickness Losses	108
3-38	Summary of Ultrasonically Measured Tube Wall Thickness Changes Occurring as a Result of Test Exposure	110
3-39	Test Panel Measurements by Metal Type	113
3-40	Test Panel Measurements	116
3-41	Comparison of Field and Laboratory Measurements (Mils)	118
3-42	Qualitative Summary of Corrosion Measurements	121
3-43	Summary of Left Side Wall Corrosion Rate Measurements (Mils/Year)	123
3-44	Furnace Gas Tap Tests Numbers Grouped by Test Conditions	124
3-45	Corrosion Rates (Mils/Yr) as Measured on the Left Wall	130
3-46	Furnace Gas Tap Data	132
3-47	Selected Furnace Gas CO Averages	135
3-48	Particulate Emission Test Results (Inlet to Precipitator)	138
3-49	Particulate Size Distribution, wt%	139

LIST OF TABLES (CONT'D)

Number	Title	Page
3-50	Summary of Boiler Performance Calculations	142
3-51	Wet Chemistry SO_2/SO_3 Analyses	143
3-52	ICPES Analysis of Coal Samples for Metals	146
3-53	Coal Analyses	147
3-54	Mass of Material Collected in SASS Cyclones	148
3-55	Organics Analysis Report	149
3-56	LC Fractionation Results	150
3-57	Organics Detected in XAD Extracts	151
3-58	Boron Analysis	153
3-59	Leachable Ions -- Neutral Extraction	154
3-60	Leachable Ions -- Acid Extraction	155
3-61	Quality Control -- Leachable Ions	156
3-62	Summary of Metal Data on Stack Emissions	157
3-63	Elemental Analysis (Baseline Operation) (Test #3)	158
3-64	Elemental Analysis (Low NO_x Operation) (Test #4)	159
3-65	Wall Measurement Summary -- Metal Loss in Mils (or Mils per Year)	165
E-1	Mass of Material Collected in Cyclones - Gulf Power Company, Crist Station, No. 7 Boiler	182
E-2	Compounds Sought in Pensacola, Florida Organics Samples	192
E-3	A-A Methods	195
E-4	Leachable Ion Analysis Scheme	204
F-1 through F-19	IR Analysis	218

NOTE: Most of the tables in the Appendixes are not numbered, and as such are not labeled or listed here.

e5358

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SUMMARY

Corrosion rates were related to control of NO_x emissions on a utility boiler in one of the first studies of its kind. Combustion modifications (CM) using existing boiler controls (no retrofits), were used to achieve 20% decrease in NO_x emissions at full load by non-standard boiler operation and up to about 50% decrease at lower loads. NO_x decrease was achieved by staging the burner zone by biasing the secondary air flow and dedicating the pulverizers serving the lower burners, to full load operation. Although there were no significant side effects from decreased NO_x operation, the tube wastage rate in the burner zone was increased enough that the boiler manufacturer feels that staged firing by itself with high sulfur coal may be a questionable means of controlling NO_x from pre-NSPS boilers.

The program which is the subject of this report is a comprehensive long term corrosion test using three methods of measuring corrosion: probes, panels, and ultrasonic mapping. Testing was done at the No. 7 boiler of the Crist Generating Station of Gulf Power Company. The unit was designed by Foster Wheeler Energy Corporation. Testing was performed by Exxon Research and Engineering Company with the cooperation of Foster Wheeler. This work was part of EPA contract no. 68-02-1415.

The purpose of the program was to predict the effects of proposed NO_x emission regulations. Crist No. 7 was not designed to meet those new emission standards, and this caused certain problems in the program. Furthermore, the program was interrupted several times by scheduled and unscheduled outages, and by planned maintenance procedures for the firing system.

Of the three methods of measuring corrosion rate, test panels were most accurate and precise, followed by ultrasonic mapping and finally test probes. The probes were the least expensive way of measuring corrosion rates and showed that corrosion rate was fastest during the first two weeks of exposure and the rate continued to decrease during the 300 to 1000 hour tests.

During the test program, NO_x and other emissions were monitored. CO was the only gaseous emission other than NO_x that was seen to be significantly affected by such control. Adverse effects of NO_x controls on CO emissions were overcome by properly choosing the air feed rate. This was made especially easy when a continuous CO monitor was installed on the boiler.

Boiler combustion controls investigated for use in NO_x reduction included:

- Secondary air registers, which were used to change air distribution within the combustion zone.
- Firing pattern, which was varied by changing the coal feed rates to the six burner rows resulting in changes in fuel distribution.

- o Load, which was varied.
- o Total air flow, which was varied.

The response of NO_x to register setting was weak. However it is still assumed that for lowest NO_x emission rates, air register should be adjusted in order to divert most of the air to the upper regions of the furnace so that the air/fuel ratios at the bottom burners are as low as safely possible.

Staged firing is an effective method of NO_x control. Proper use of this technique involves reduction of fuel feed to the top burners, (and adding fuel to the bottom as necessary to maintain load), so that the top burners are operated as fuel lean as possible. This means that the fuel/air ratio at the top burners should be made as low as possible. In the extreme case, when load demand permits, fuel should be shut off completely to one or more top burner rows so that only air flows through these burners. An alternate and more effective way of staging is by installing separate over-fire-air (OFA) ports. This is not easily done as a retrofit, but was part of standard design on many early NSPS boilers.

NO_x emissions decrease when load is reduced, but since boilers usually have very little freedom to vary load, load reduction should be considered only as a last resort for NO_x control. Instead, load is usually set according to customer demand for electricity. In rare cases, boilers have been derated when other attempts to reduce NO_x emission rates failed.

Perhaps the best method for decreasing NO_x emission rates is by decreasing the amount of air available to produce it. One method is cutting back on the excess air used in the combustion process. Excess air is measured as percent oxygen in the flue gas. When decreasing excess air for NO_x control, it should be done only to the point where CO emissions begin to increase. This means that a CO monitor must be used as an aid to NO_x control. Also, unburned carbon on fly ash must be monitored.

Other emissions measured included SO_2/SO_3, particulate matter in the flue gas by both mass and size distribution, and emissions of organic matter and trace elements using the "Source Assessment Sampling System" (SASS) train. Boiler performance was also measured.

Testing for low-NO_x combustion modification side effects received increased attention during these investigations including the effects of low-NO_x firing on particulate mass and size distribution, toxic and trace element pollution, sulfur oxide emissions, boiler performance and furnace tube corrosion. Side effect evaluation testing, with the exception of stack environmental assessment studies using EPA's SASS train, followed the same general pattern employed in tests on over 35 pulverized coal fired boilers tested to date by Exxon under EPA sponsorship (3,7,8). Results in the current program by and large confirm previous results. At the levels of NO_x decrease practiced in this program, the analysis shows that where differences may exist in emissions, boiler operation, etc. between baseline and low-NO_x firing conditions, the magnitude of these differences is minimal and no appreciable effect on operation or performance of the boiler, dust collectors, etc. would be expected. However, the NO_x reduction methods used (fuel/air biasing and reduced excess air firing) will limit boiler flexibility and may not be as applicable to coals other than that tested. The potential for increased furnace tube corrosion is presently being further studied by Exxon in another program where NSPS boilers are being evaluated.*

Since the influence of NO_x controls on corrosion rates in the boiler was of special interest in this test program, several methods were used to assess corrosion and the potential for corrosion within the boiler. These included:

- Furnace gas taps - Analysis of furnace gases for chemically reducing properties.
- Corrosion probes - Exposure of small samples of boiler tube wall material through inspection doors and into the furnace.
- Corrosion panels - Removing specially installed sections of the boiler wall for analysis.
- Ultrasonic mapping - Measurements of tube wall thickness during periodic outages.

These measurements were done under normal, as-found ("baseline") boiler operating conditions, and also under "low-NO_x" conditions.

Of the furnace gases analyzed, O_2 and CO were examined in detail since they indicate corrosive reducing environments. In all cases, CO concentrations were high, as expected, where O_2 concentrations were low. Generally, one would expect to see decreasing CO concentrations (depletion through burn-out) with increasing elevation (further downstream) in the boiler. In many of the tests reported herein, staged combustion was used to elongate the flame to achieve lower flame temperatures. This caused CO concentrations to remain high further downstream in the flue. But even with the most extreme staging, CO depletion was always achieved upstream of the boiler's economizer outlet. No other strong relationship between CO and height in the boiler was apparent.

The CO/O_2 ratio within the furnace was generally higher for low-NO_x firing patterns than for baseline conditions, indicating a greater potential for corrosion at low-NO_x conditions than for baseline. For "as-measured" furnace gas composition, the difference between baseline and low-NO_x conditions was most noticeable in the CO concentrations along the wall at the top burner elevation. Here, the CO readings were higher during low-NO_x operation than during baseline tests. (Not much difference was seen in the CO concentration at other elevations.) And, not suprisingly, for this region of the furnace, corrosion rates (as determined by ultrasonic wall thickness maps) were higher at low-NO_x conditions than at baseline.

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*"Long Term Optimum Performance/Corrosion Tests of Combustion Modifications for Utility Boilers" EPA Contract No. 68-02-2696.

Wall thickness measurements also showed that under baseline operation, there was only a small difference in corrosion rates between burner and non-burner elevations. However, under "low-NO_x" operation, the burner area lost more metal than the non-burner zone. Furthermore, the burner zone loss was greater under low-NO_x than it was under baseline. However, in the non-burner zone the corrosion rate under baseline was almost triple the low-NO_x rate.

Under baseline, wall thickness measurements showed significant corrosion on only the right wall. This, according to the boiler's manufacturer, may have been a result of previous unit operation with the left burner registers more open than the right ones, thereby resulting in a reducing atmosphere in the right side wall. But under low-NO_x, all the walls (by the "half wall method" of analysis) showed significant corrosion except for the non-burner elevations of the right and rear walls. Furthermore, when comparing low-NO_x with baseline, only the left wall showed increased corrosion.

Testing under this program was designed to help evaluate methods of minimizing tube wall corrosion rates if a potential problem was uncovered. To this end, two types of metals were used in the test panels so that the corrosion resistance of each could be evaluated. Analysis of these replaceable wall tube test sections (corrosion panels) showed that steel type SA 213 experienced an insignificantly smaller amount of corrosion than SA 210. During low-NO_x operation, burner-zone panels corroded faster than non-burner-zone panels.

For the panels in the burner zone, more corrosion occurred during low-NO_x than during baseline operation. The opposite was true for panels in non-burner zones.

Corrosion probe data show that the rate of metal loss is fastest when the probe is first exposed into the furnace, but slows down as exposure time increases. During very short exposures (30 hours), burner-zone probes corroded faster than non-burner-zone probes under both baseline and low-NO_x conditions. But longer term exposures (240-1000 hours) did not show significant corrosion rate differences between burner and non-burner zones, or between baseline and low-NO_x operation.

Generally, it can be said that NO_x was decreased by about 20% by using the boiler's existing combustion control hardware, and that no immediate adverse side effect resulted. However, the boiler's manufacturer feels that wastage rates on the boiler's side walls indicate that long-term operation under the reduced NO_x biased-firing test conditions could potentially result in a corrosion problem.

1. INTRODUCTION

Oxides of nitrogen (NO_x) react chemically, in the presence of sunlight, with organic gases, and other pollutants and produce the brown smoggy haze commonly occurring in densely populated areas. When NO_x concentrations in ambient air rise above 5 parts per million (ppm), a health hazard may exist. (This threshold can be as low as 0.1 ppm NO_x for people who have asthmatic conditions.) Persons exposed for four hours to such concentrations may experience temporary narrowing of air passages, breathing difficulty, and other respiratory related ailments (1). (One study (2) suggests that this danger threshold for NO_x concentrations may be even lower.) NO_x is also partially responsible for "acid rain" as it reacts in the atmosphere to form nitric acid (HNO_3). Hence, NO_x has been classified as a major pollutant and a great deal of effort has been aimed at its abatement. Typically, NO_x is a product of combustion. It is formed by a reaction involving nitrogen found in either the fuel (fuel NO_x) or the air sustaining combustion (thermal NO_x). The latter reaction is significant only at high temperatures (hence the word "thermal").

In 1969, Esso (now Exxon) Research and Engineering Company completed Phase 1 of a systems study for the National Air Pollution Control Administration (NAPCA, now the United States Environmental Protection Agency - EPA) in which sources of NO_x were identified. The study showed that stationary sources accounted for at least half of all oxides of nitrogen (NO_x) and that more than a third of that half was due to utility boilers used for production of electricity (3). A more recent report (4) indicates an even higher NO_x contribution from utility boilers. Even with tight controls and regulations, NO_x is expected to continue to increase (5).

The Phase 1 systems study (3) recommended methods for NO_x control at stationary sources with emphasis on utility boilers. Under a follow up contract (Phase 2) with the United States Environmental Protection Agency (EPA) (6), Exxon tested, at utility boilers, many of the NO_x control methods that were proposed in the original systems study. During these field tests, effects of various operating parameters were investigated while gaseous emissions, including NO_x, were measured and related to the operating mode of the boilers. These changes in operating mode, also called "combustion modifications" (CM), included lower fuel/air ratios at certain upper burners (staged combustion), decreased excess air flow, flue gas recirculation (FGR), and changes in air preheat temperature, load, and burner tilt.

Seventeen boilers of various designs and fuels were tested including seven coal-fired units. Boiler manufacturers participated in the tests at three of the seven coal-fired units in order to assess the side effects of low NO_x operation, including: thermal efficiency, slagging, and other emissions.

Preliminary data from two of the seven coal-fired units showed that coal-fired boilers were responsive to CM for NO_x control. The limited data from the three tests involving boiler manufacturers showed no adverse side effects due to CM for low-NO_x operation. (But one side effect not studied was boiler tube wall corrosion rate.)

A new program was initiated to study coal fired boilers in more detail. Under the new program, sponsored by EPA, CM for NO_x control was evaluated at twelve coal fired utility boilers with close attention to side effects. The resulting report cited NO_x reductions of 25 to 60% (7) with either combustion modification or load reductions, or both, but the report concluded that still more testing was required to evaluate corrosion and slagging effects of low-NO_x operation.

The EPA and the Electric Power Research Institute (EPRI) jointly funded an Exxon field test program in which the work scope was broadened to determine the effects of CM techniques on pollutant emissions and combustor performance for a variety of combustion systems and fuels. Included were boilers, and gas turbines with continuing emphasis on coal-fired utility boilers. One boiler was retrofitted with specially designed "low-NO_x" burners. Under the new EPA contract, 14 combustion systems were tested. One publication written under that contract concerning seven of the tested units reported NO_x reductions of about 40% without hardware modifications (8), but possibly including decreased load, and decreased excess air while still remaining within design limits for the boiler.

Since 1971, EPA rules have limited NO_x emission rates and set other performance standards for new stationary sources. The field test program showed CM to be a relatively easy way of meeting these new source performance standards (NSPS). In fact, staged combustion, a CM proposed and tested by Exxon and others is now used by two of the four major boiler manufacturers to meet NSPS NO_x emission limits.*

But low-NO_x operation by CM brings with it the possibility of increased slagging and furnace tube wall corrosion, especially with high-sulfur (S) coals. Tests at TVA's Widows Creek generating station, for example, indicated a possible problem. But testing at APS's Four Corners Station on low S coal gave conflicting results. Clearly, more testing was needed. Consequently, EPA emphasized the desirability of NSPS type field research even though no wall-fired boilers, designed to meet NSPS for NO_x emissions were yet available.

Gulf Power, which had participated in earlier EPA sponsored studies, recognized the need for a comprehensive study, and agreed to cooperate by making the No. 7 boiler at their Crist generating station in Pensacola, Florida, available for a long-term test.

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*It should be noted, however, that the manufacturer of the Crist #7 unit no longer offers overfire air ports as original equipment on new NSPS boilers. All NO_x control is achieved with low-NO_x burners which are now a standard offering for such applications. This manufacturer (FW) does not recommend the use of overfire air as a retrofit to existing pre-NSPS units.

Thus, Crist No. 7, one of the last boilers to be tested under this EPA funded contract, became the first* to be extensively tested for corrosion rates relative to NO_x emissions. Corrosion rate was measured in several ways: by corrosion probes, removable tube wall sections (called corrosion panels), and by ultrasonic mapping of furnace wall thickness. These techniques are explained in the body of this report.

The test plan was statistically designed to include sufficiently large numbers of measurements so that even small changes in corrosion rates could be identified. This was to be done while providing for evaluation of measurement and calibration errors. Provisions were also made to account for any bias introduced by cleaning procedures on tubes prior to measurement.

Samples of the tube wall were removed and sent to the laboratory for examination and metallurgical evaluations of corrosion mechanisms.

While the Crist corrosion tests were underway, the boiler was also tested for emissions and performance in the same way as other boilers in the programs already mentioned.

This report covers testing at Crist No. 7 and describes the effect of low-NO_x operation on boiler performance.

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*Under EPA Contract #68-02-2696, Exxon will be testing corrosion rates at several new boilers specifically designed to meet NSPS.

2. FIELD STUDY PLANNING PROCEDURES

This section describes the major steps involved in planning and conducting the long-term corrosion field study on Gulf Power Company's Crist No. 7 boiler with the participation and cooperation of Foster Wheeler Energy Corporation. Field study planning steps included selection of a test boiler (with participation of EPA, equipment manufacturers and utility boiler operators), and designing the test program strategy with special emphasis on effective methods of measuring furnace tube, hot-side corrosion. Methods of gaseous emission testing were similar to those developed and applied in ER&E's "Systematic Field Study" (14). Particulate sampling, corrosion probe measurement and performance measurements used were also based on methods used in ER&E's previous field studies (8). The long-term corrosion study reported here was part of a larger ER&E program involving boilers firing coal, coal-oil and coal-gas mixed fuel as well as gas and oil fired power generating gas turbines (8).

2.1 Selection and Description of Test Boiler (Crist No. 7)

A cooperative planning effort by Exxon Research, EPA, EPRI and boiler manufacturers (Babcock and Wilcox, Combustion Engineering and Foster Wheeler) resulted in the selection of the test boiler. This involved developing boiler selection criteria, reviewing boiler manufacturer's candidate boilers meeting the criteria, selecting a tentative list of boilers for detailed field meetings and final selection and scheduling of test programs as described in a previous report (7).

Criteria for selection of this coal fired boiler were classified into five groups: (I) boiler design factors, (II) boiler operating flexibility, (III) boiler measurement and control capability, (IV) boiler operating management policy concerning research and operating practices and (V) logistic and scheduling considerations.

A wall-fired boiler representing current design practices, burning high sulfur coal (known to influence corrosion), and having an output capacity of at least 150 MWe was desired. The boiler desired was to have the capability of meeting the Federal NSPS of 0.7 lbs of NO_x emitted per 10^6 Btu (301 nanograms per joule) heat input, under staged combustion, with only a small reduction in load. The boiler operator was to be willing to have specially constructed tube wall, test panels inserted in the sides of the test boiler for corrosion measurement purposes.

A compromise was made in that it was recognized that the boiler chosen might be unable to achieve the 0.7 lb/million Btu (301 ng/J) goal at high load with the intended combustion modifications.

Another key requirement was the support of the utility operating management for the research program. This support included providing the necessary technical, supervisory and operating personnel for both planning and conducting the test program. In this test program, the enthusiastic support and encouragement of Mr. George O. Layman, Manager of Production for Gulf Power Company and the cooperation of Mr. C. R. Lee, Crist Station Superintendent were very beneficial.

The prime question to be answered in this test program was whether combustion modification, particularly for boilers fueled with high sulfur coals, would result in accelerated wall tube corrosion rates. Short term corrosion rate measurements by probes have demonstrated that staged firing of coal does not result in catastrophic corrosion tendencies; however, actual wastage rates could not be determined from these measurements (8). Gulf Power, a participant in previous EPA sponsored studies conducted by Exxon Research, recognized the need for a comprehensive study and agreed to cooperate by making Crist No. 7 unit available for this long term test program.

The Crist Power Plant is located on the Conecuh River north of Pensacola, Florida. The plant consists of seven boiler/turbine-generator systems with a combined output of 970 MW. Units 1 and 2 began operation in the mid-1940's. Unit 3 began operation in the early 1950's and Units 4 and 5 in the late 1950's. Unit 6 began operation in the late 1960's and Unit 7 in 1973. Unit 7 has a rated output of 500 MW.

Crist No. 7 is a pulverized-coal-fired boiler built by Foster Wheeler Energy Corporation. It is a horizontally-opposed, natural circulation, radiant, reheat type steam generator. The furnace has 24 burners (12 on each of the front and rear walls), arranged in three rows of four on each wall. There are six pulverizers, each feeding one row of four burners. This unit was originally designed with a pressurized furnace but was converted to balanced draft operation before the conclusion of this test program. Curtain air slots were retrofitted to the rear wall hopper to minimize slag formation. Foster Wheeler uses a more advanced form of air injection, known as Boundary Air, for slag, CO, and tube wastage control in which slots in the hopper throat and along the hopper slope and ports on firing walls inject combustion air from the windbox along the hopper and burner zone waterwall tube surfaces. The partial installation of such an air injection system on Crist 7 (to clear up a slag problem on the rear slope of the hopper) was not expected (according to this boiler's manufacturer) to have any measurable effect on this study's outcome. Nevertheless, it was desirable to determine, to the extent possible, the effect that this air injection system (installed in the rear slope of the hopper) might have in minimizing corrosion within the Crist No. 7 boiler.

Crist No. 7 has a rated capacity of 1.64×10^6 kg of superheated steam per hour (3.6×10^6 lb/hr) at 17.2 MPa (2500 psi) and 810K (1000°F). Steam temperature is controlled by spray attemperation and flue gas proportioning dampers. Its electric rating is 500 MW.

Flue gas cleaning equipment on Crist No. 7 consists of a cold side electrostatic precipitator (ESP). The flue gas exits the boiler in two ducts, each having a separate ESP. After leaving the ESP's, the ducts are combined and exit to the stack. Figure 2-1 shows a cross section of the boiler.

2.2 Test Program Strategy

The program strategy used to test the Crist No. 7 boiler consisted of four phases: (I) Defining the optimum operating conditions for NO_x emission control, without apparent adverse side-effects in a short-term, statistically designed field test program; (II) operating the boiler for two days under the "low-NO_x" conditions determined during the optimization phase. This was for assessing boiler operability problems such as excess slagging or steam temperature control difficulties; (III) operating the boiler for 300 hour sustained runs under both baseline and low-NO_x operating conditions for corrosion probe testing, particulate testing and obtaining boiler performance measurements; and (IV) long-term, sustained baseline and low-NO_x operations with premeasured and metallurgically characterized wall tube test panels inserted into the boiler walls for corrosion measurements. References cited in the introduction to this report describe in some detail the evolutionary development of this four phase strategy.

The test program was tailored specifically to encompass the operating flexibility of the Crist No. 7 boiler. The up-to-date comprehensive information necessary to plan each of the four test phases of the program were obtained at field meetings with all interested parties. More information about the test schedule may be found in Appendix A.

2.3 Corrosion Measurements on Fireside of Furnace's Water Walls

Combustion modification techniques used to reduce nitrogen oxide emissions in boilers, such as staging the combustion process and reducing excess air levels used for combustion, can produce a net reducing environment in the lower region of the furnace, especially in the burner area. Considerable concern was expressed that this effect potentially may increase the corrosion rate in the tubes forming the walls of the furnace, since high tube wastage was experienced in furnace tubes in areas of local reducing environments during the early days of the development of pulverized coal firing for utility boilers.

Three methods were used to evaluate corrosion rates within the furnace.

- Corrosion probes
- Ultrasonic measurements of wall thickness
- Corrosion panels: removal of furnace wall sections

Besides these 3 methods, furnace gas taps were used to give local furnace gas composition information for correlation with measured corrosion rates. For example, if a certain furnace gas tap showed a potentially corrosive mixture of gases, then special attention could be given to the corrosion measurements in that part of the

FOSTER WHEELER

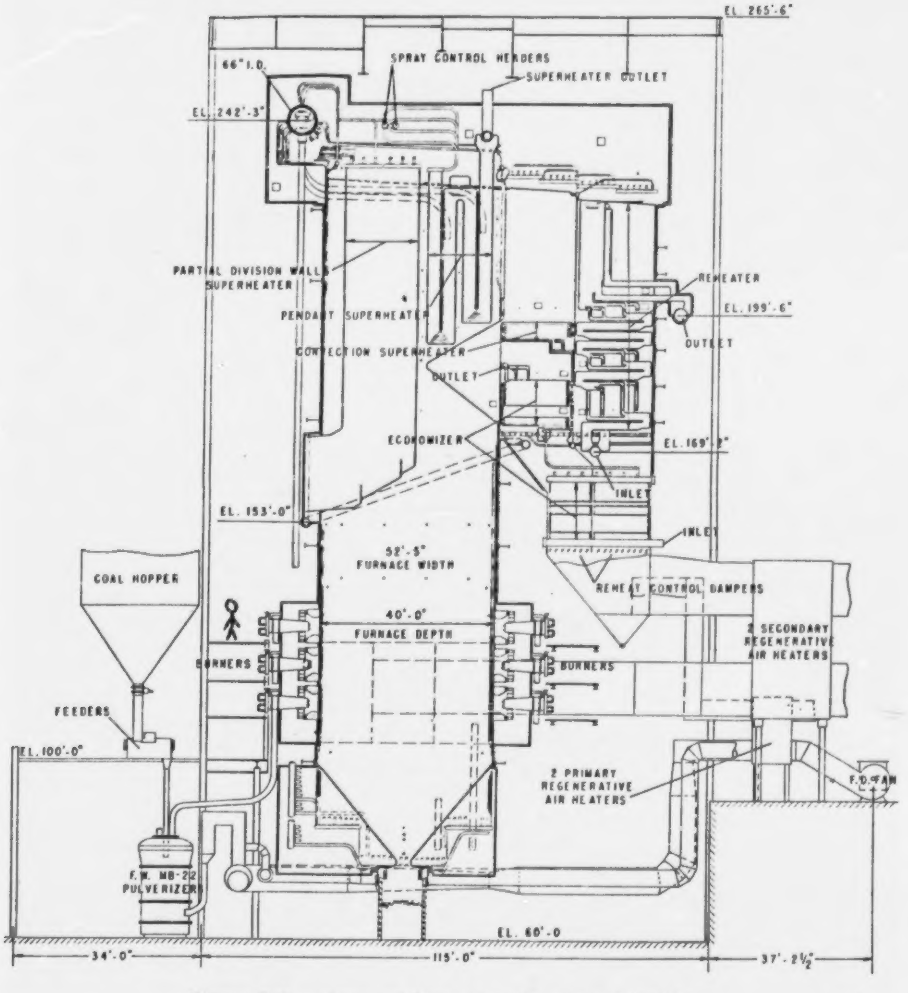

EL. 265'-6"
SPRAY CONTROL HEADERS
SUPERHEATER OUTLET
66" I.D.
EL. 242'-3"
PARTIAL DIVISION WALLS SUPERHEATER
PENDANT SUPERHEATER
CONVECTION SUPERHEATER
OUTLET
REHEATER
EL. 199'-6"
OUTLET
ECONOMIZER
EL. 169'-2"
INLET
EL. 153'-0"
INLET
52'-5" FURNACE WIDTH
COAL HOPPER
REHEAT CONTROL DAMPERS
40'-0" FURNACE DEPTH
2 SECONDARY REGENERATIVE AIR HEATERS
BURNERS
BURNERS
FEEDERS
EL. 100'-0"
2 PRIMARY REGENERATIVE AIR HEATERS
F.D. FAN
F.W. MB-22 PULVERIZERS
EL. 60'-0
34'-0"
115'-0"
37'-2½"

Figure 2-1. Cross section of Crist, Unit 7 boiler.

Name .... GULF POWER COMPANY .... Design Pressure 2875 psig ....
Location .... PENSACOLA FLA. CRIST STEAM PLANT UNIT NO. 7 .... Final Steam Temperature 1000/1000F ....
Capacity 3817.5M lb/hr Type REHEAT ....

NOT REPRODUCIBLE

furnace wall. The next three sections of this report explain these three methods of determining boiler corrosion rate.

2.3.1 Corrosion Probes

One way of evaluating boiler corrosion rate is to insert pieces of boiler tube wall material into the furnace through inspection doors. Corrosion rate can then be determined through weight loss analysis. This was the basis for the Crist corrosion probe testing. At Crist No. 7, for each corrosion probe test, four corrosion probes were used simultaneously. Each probe was inserted through a different furnace inspection door and all were exposed to the furnace gases for the same period. Two were in the burner zone and two were high above the burners, as controls, where corrosion was not expected to occur (see Figure 2-2). Many such tests were run covering various exposure periods from 24 to 1000 hours. The tests also covered at least two different boiler operating modes (baseline and low-NO_x). Each corrosion probe actually contained more than one type of steel to allow evaluation of each material's resistance to corrosive attack.

This wide variety of test variables allowed corrosion rate to be determined as a function of any of the following variables:

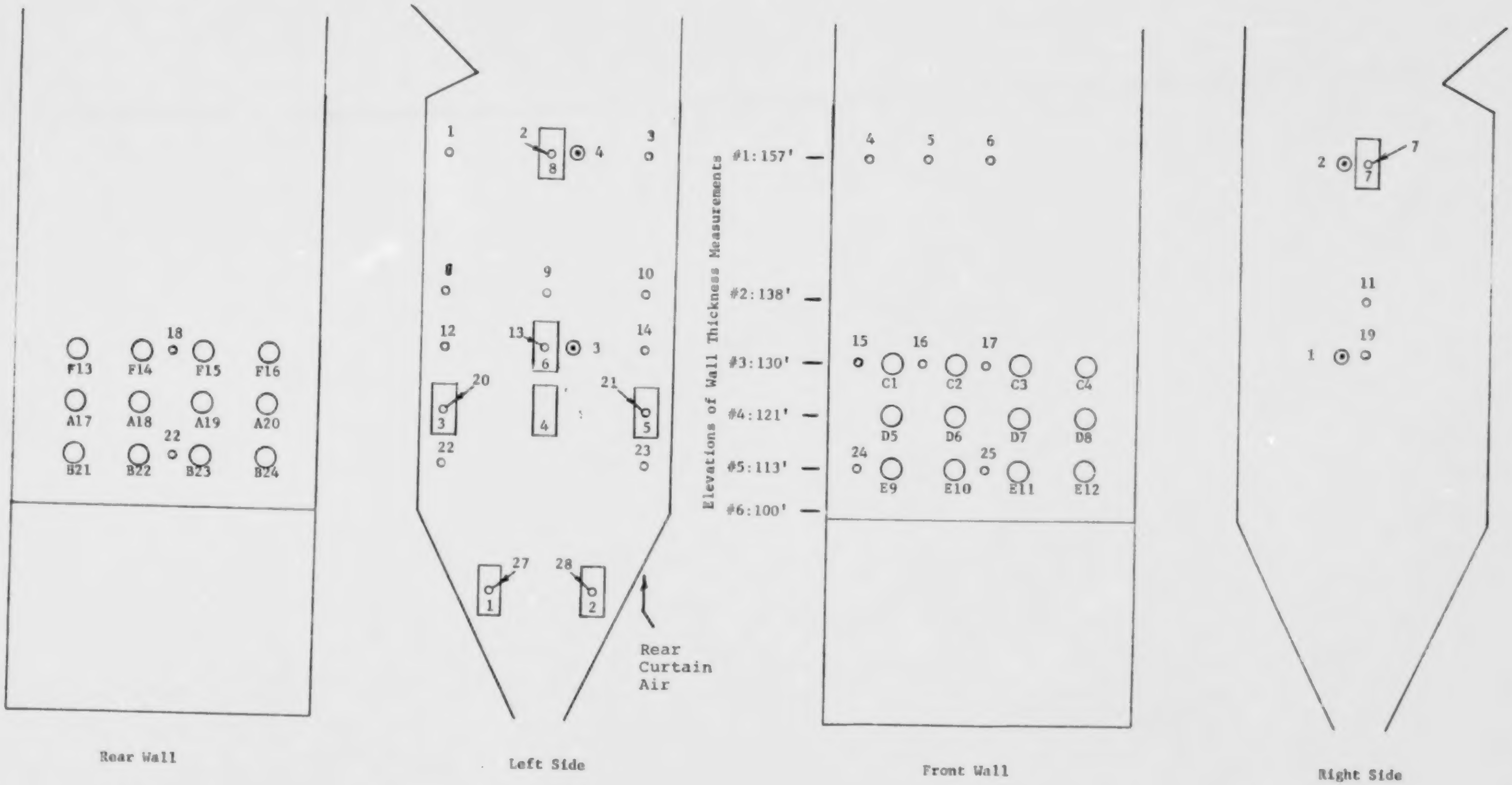
- Location within the boiler
- Boiler mode of operation
- Time (corrosion rate actually changed with time)
- Composition of metal being corroded

Figures 2-3 and 2-4 show the corrosion probe design. Notice that each corrosion probe consisted of three corrosion coupons. About half of the corrosion coupons were made from ASTM steel, type 192, a low carbon steel.

Each of the three coupons (including both 192 and 210 materials) used on each probe assembly contained thermocouple (TC) wells. Two thermocouples (TC) were installed in each probe assembly. The coupons were air-cooled to 625-725°F (329-385°C), the typical operating range of furnace wall-tubes.

At the beginning of an exposure period, which typically lasted either 30, 300, or 1000 hours, the cooling system was adjusted by sliding the central air rod in or out as necessary until both thermocouples showed the same temperature. Then, one TC was connected to a strip chart recorder and the other to the system that controlled the cooling air.

After many hours of exposure, the two TC's would often not read identical temperatures because of uneven slag coatings, or local air leaks in the probe. It was not unusual to find the strip chart recorder showing a temperature several hundred


Rear Wall
F13
F14
F15
F16
A17
A18
A19
A20
B21
B22
B23
B24
18
22
Left Side
1
2
8
4
3
8
9
10
12
13
6
3
14
20
3
4
21
5
22
23
27
1
28
2
Rear
Curtain
Air
Elevations of Wall Thickness Measurements
#1:157'
#2:138'
#3:130'
#4:121'
#5:113'
#6:100'
Front Wall
4
5
6
15
16
17
C1
C2
C3
C4
D5
D6
D7
D8
24
25
E9
E10
E11
E12
Right Side
2
7
7
11
19
1

Key:

○ Furnace Gas Tap

▯ Corrosion Panel

⊙ Corrosion Probe

◯ Burner

Figure 2-2. Boiler layout
(as seen by observer facing the
boiler from outside).

Note: Figure is not to scale.

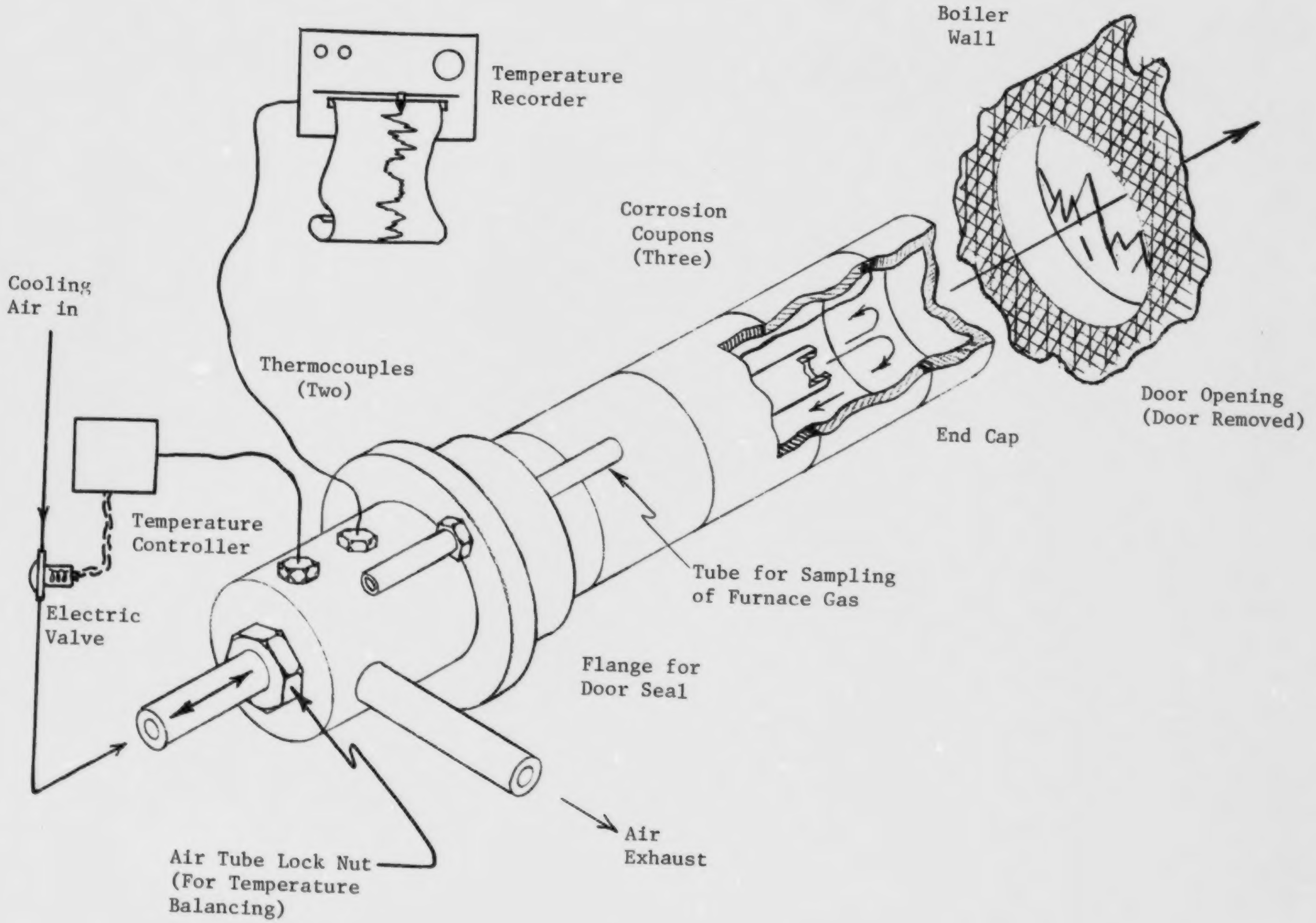

Boiler
Wall
Temperature
Recorder
Corrosion
Coupons
(Three)
Cooling
Air in
Thermocouples
(Two)
Door Opening
(Door Removed)
End Cap
Temperature
Controller
Tube for Sampling
of Furnace Gas
Electric
Valve
Flange for
Door Seal
Air
Exhaust
Air Tube Lock Nut
(For Temperature
Balancing)

Figure 2-3. Corrosion probe.

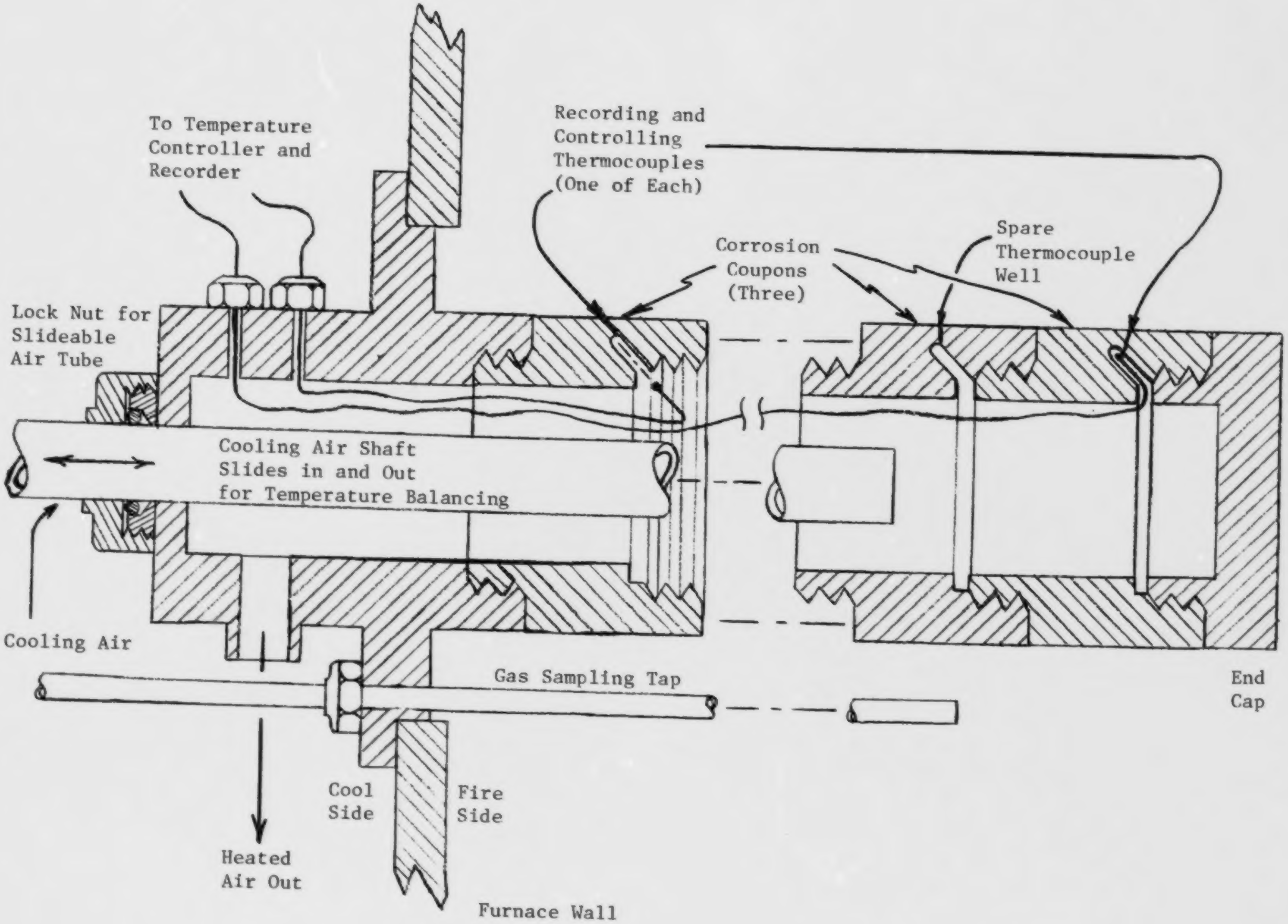

To Temperature Controller and Recorder
Recording and Controlling Thermocouples (One of Each)
Corrosion Coupons (Three)
Spare Thermocouple Well
Lock Nut for Slideable Air Tube
Cooling Air Shaft Slides in and Out for Temperature Balancing
Cooling Air
Gas Sampling Tap
End Cap
Cool Side
Fire Side
Heated Air Out
Furnace Wall

Figure 2-4. Corrosion probe (cross sectional view).

degrees different from the set point on the air controller. Hence, the probes required frequent attention and rebalancing during a test.

Prior to assembly onto the probe, each coupon was stamped with an identifying mark, cleaned in acetone and isopropanol, and weighed to ±0.0001 grams.

In previous studies "pickling" (mild acid coating) and accelerated rate (high temperature) testing were employed. The resulting data contained considerable scatter. At Crist, coupon exposure conditions (temperature, geometry, location, etc.) were as similar as possible to the environment of real furnace tubes. Exposure times of 30 hours, 300 hours and up to 1000 hours were employed under both baseline and low-NO_x conditions to determine initial, intermediate, and longer term corrosion effects. Special ports (doors) were installed in the furnace for the installation of the probes in the most desirable areas. Two of these ports (see Figure 2-2) were located in the middle of the sidewalls within the burner zone (elevation 129.8 ft) in what was believed to be the most corrosion prone area. Two others were located at the middle of the sidewalls but in the upper furnace area (elevation 157.8 ft) outside of the expected corrosion area, in order to provide "control" data.

After exposure, each probe assembly was disassembled and the coupons were cleaned up in the laboratory to remove slag deposits. Cleaning (dry honing), was done in an ultrasonic vibrating bath containing glass beads. Then the coupons were weighed.

This final weight was compared to the initial weight and total metal loss was determined. Since the exposure time was known, the corrosion rate could then be calculated.

2.3.2 Ultrasonic Furnace Tube Wall Thickness Measurements

Considerable effort went into planning the ultrasonic furnace tube wall thickness measurements. Considerations for determining where to make the measurements and how many measurements to make included the following:

1. Location of most likely and least likely corrosion areas within each wall.
2. Precision and accuracy of the ultrasonic measuring instruments.
3. The necessity of including methods for obtaining accurate estimates of changes, if any, in normal corrosion rates due to necessary tube cleaning before measurement (bias).

4. Additional measurements for quality control purposes.
5. Costs of cleaning tubes, ultrasonic measurement and necessary supervision.

Boiler manufacturer and operating experience have indicated that the middle area of boiler side walls, within and just above the top row of burners, is most likely to experience the highest rate of tube wastage. Consequently, four of the six ultrasonic measurement levels were located at the center of the three burner elevations and about 8 1/2 feet (2.59 m) above the centerline of the top burner level. The "control" levels were 28 feet (8.53 m) above the centerline of the top burner level and about 13 feet (3.96 m) below the bottom burner row (see Figure 2-2). Measurements were more highly concentrated within the middle of the side wall burner area than near the furnace corners or below and above the burner elevation.

(Appendix G contains a description of the acoustic instrument used to measure tube wall thickness.)

Since sandblasting (or wire brushing), necessary to clean the ash and slag coating off the tube (for accurately measuring tube wall thickness), may remove a protective coating and thus cause increased metal loss, special precautions had to be taken to avoid biased results and conclusions. A single measurement was made on the sidewalls on a given tube at a given level or there were two measurements (just above and below) with the center space not cleaned or measured. The average of the above and below measurements provide an unbiased estimate of the "after" center spot while the "before" center spot measurement is also unbiased. This procedure was used on the boiler walls to provide assurance that the furnace tube cleaning and measurement process did not result in biased corrosion estimates or conclusions even though the cleaning process does result in changing the normal corrosion rate up or down in either (or both) reducing or oxidizing atmospheres. Section 3.2.2 provides a detailed description of the statistical tests used to determine if biased measurements resulted from the cleaning process.

Special precautions were taken by Foster Wheeler to assure that the "after" measurements were taken at the same location as the "before" measurements.

Ultrasonic tube wall thickness measurements were made at six different levels (elevations) (see Figure 2-2): (1) 157 feet, 8 inches, (2) 138 feet, 2 inches, (3) 129 feet, 8 inches (top burner row centerline), (4) 121 feet, 2 inches (middle burner row centerline), (5) 112 feet, 8 inches (bottom burner row centerline), and (6) 93 feet (ash hopper area). Four sets of ultrasonic wall tube measurements were made: (1) May, 1976 (before baseline operation, (2) October, 1976 (after baseline operation), (3) October, 1977 (middle of low-NO_x operation) and (4) May, 1978 (end of low-NO_x operation).

2.3.3 Tube Wall Test Panels

Each of the boiler manufacturers (Foster Wheeler, Combustion Engineering, Babcock and Wilcox and Riley Stoker) in discussions held in order to properly plan a long-term corrosion study, indicated that the most definitive assessment of potential hot side, tube wall corrosion would be obtained through use of test panels (premeasured and metallurgically characterized) installed as integral sections of the furnace water walls.

Since boiler walls are large and vulnerable areas and difficult to define accurately in advance of exposure, the panels were largely concentrated on one of the furnace sidewalls. Specifically, the eight test panels were located as listed below (Table 2-1), and shown in Figure 2-2.

TABLE 2-1

TEST PANEL LOCATIONS

Panel Number	Sidewall	Elevation	Distance from Center of Sidewall
1	Left	93 feet	10 feet (3.05 m) to right
2	Left	93 feet	10 feet (3.05 m) to left
3	Left	121 feet, 2 inches	15 feet (4.57 m) to right
4	Left	121 feet, 2 inches	Centerline
5	Left	121 feet, 2 inches	15 feet (4.57 m) to left
6	Left	129 feet, 8 inches	Centerline
7	Left	157 feet, 8 inches	Centerline
8	Right	157 feet, 8 inches	Centerline

Panels (or sections of panels) were installed or removed or measured during each of the four outages in which wall thickness measurements were made. See event chart (Figure 2-4.1).

The initial panels were 5 tubes wide by five feet (1.52 m) tall and contained thermocouples for monitoring boiler wall temperatures. Tube dimensions were the same as in the normal boiler walls. That is: 3 inch (7.6 cm) (OD) tubes having a wall thickness of about 1/4 inch (0.6 cm) and a 1/4 inch (0.6 cm) fin or web between adjacent tubes.

Two different ASTM steel types were used in the construction of the panels and replacement sections. The panel tubes were alternately of SA 210 Grade A1, and SA 213 Grade T2, with the first, third, and fifth tube being SA 210, the usual boiler tube wall material, and the second and fourth being SA 213. This was done to allow evaluation of a more corrosion resistant steel along with the usual boiler tube wall material.

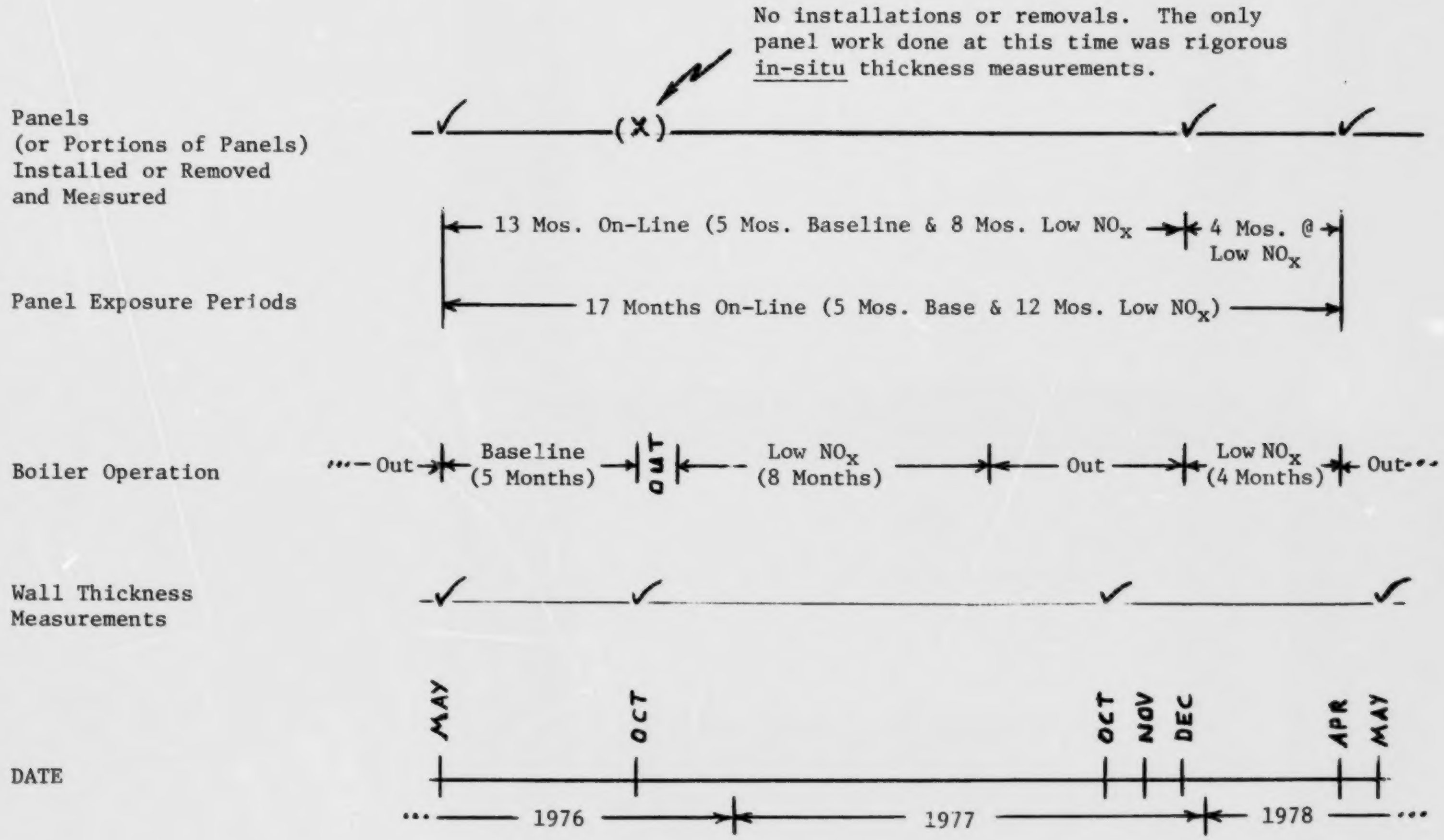
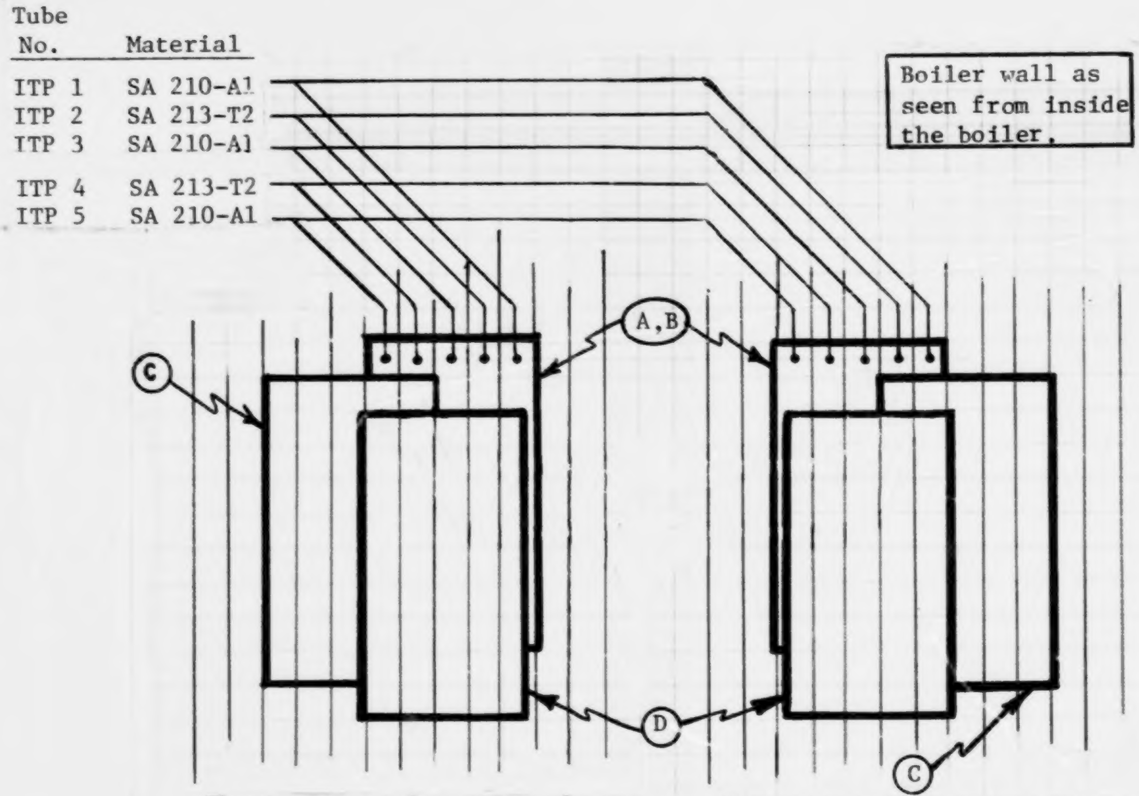

No installations or removals. The only panel work done at this time was rigorous in-situ thickness measurements.
Panels (or Portions of Panels) Installed or Removed and Measured
(X)
13 Mos. On-Line (5 Mos. Baseline & 8 Mos. Low NO_x
4 Mos. @ Low NO_x
Panel Exposure Periods
17 Months On-Line (5 Mos. Base & 12 Mos. Low NO_x)
Boiler Operation
Out
Baseline (5 Months)
OUT
Low NO_x (8 Months)
Out
Low NO_x (4 Months)
Out
Wall Thickness Measurements
DATE
MAY
OCT
OCT
NOV
DEC
APR
MAY
1976
1977
1978

Figure 2-4.1. Event Chart: Panel exposure & wall thickness measurements.


Tube No.
Material
ITP 1 SA 210-A1
ITP 2 SA 213-T2
ITP 3 SA 210-A1
ITP 4 SA 213-T2
ITP 5 SA 210-A1
Boiler wall as seen from inside the boiler.
C
A,B
D
C

Three-step replacement scheme for panels 1, 4, 6, and 7

Three-step replacement scheme for panels 2, 3, 5, and 8

FIGURE 2-4.2. CORROSION TEST PANEL INSTALLATION AND MEASUREMENT SCHEDULE*

* The drawing shows the three-step replacement scheme used for each panel, and specifically shows which tubes were replaced for each panel. (The left figure shows the three steps for panels 1, 4, 6, and 7 while the figure on the right applies to each of the other four panels.) Note that symmetry of the work performed on panels 1, 4, 6, and 7 is opposite to that for panels 2, 3, 5, and 8.

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* See notes on next page.

Schedule Notes for Figure 2-4.2

The following pertains to each of the eight panels. The initial letters refer to labels on Figure 2-4.2.

A May 1976. Start of baseline operation exposure tests. A 5-tube section of the original boiler wall (SA 210-A1) was cut out and replaced with the 5-tube corrosion panel consisting of three SA 210-A1 tubes and two SA 213-T2 tubes, alternating. This newly installed section (known as the initial test panel (ITP)) was carefully measured for tube wall thickness.

B Oct. 1976. The 5-tube ITP was measured for the second time, in-situ, after 5 months of baseline exposure. No tubes were installed or removed at this time.

C Dec. 1977. A 5-tube section of the boiler wall was removed and sent to the laboratory for analysis. This consisted of two tubes from the ITP (one SA 210-A1 and on SA 213-T2) after 13 months of mixed operation (5 mos baseline + 8 mos low-NO_x) and three of the original (SA 210-A1) boiler wall tubes after ~5 yrs of exposure. A new pre-measured 5-tube section (all SA 210-A1) of wall was used to replace these tubes and restore this section of the boiler wall to its original material (SA 210-A1). This new section is known as the replacement panel (RP).

D April 1978. The three remaining ITP tubes (two SA 210-A1 and one SA 213-T2, installed May 1976) as well as two tubes from the replacement panel (RP 1 and RP 2, both SA 210-A1, installed Dec. 1977) were removed and sent to the laboratory for analysis after 4 months of low-NO_x exposure for the two RP tubes and 17 months of mixed exposure (5 mos. baseline + 12 mos. low-NO_x) for the 3 ITP tubes. These 5 removed tubes were replaced by 5 new pre-measured tubes (all SA 210-A1) to restore the boiler to its pre-test condition.

On subsequent outages, portions of each original panel were measured in place, or removed for analysis. The resulting void was filled with a new panel section. This process continued on subsequent outages thus providing for evaluation of many different exposure times in each section of the boiler wall hosting a panel. Figure 2-4.2 shows a typical installation and measurement plan for a panel.

At the conclusion of the test, all panels and panel sections were cut out of the boiler and the walls were restored to their original condition.

2.4 Gaseous Sampling and Analysis System

2.4.1 Flue Gas at Economizer Outlet

Figure 2-5 shows the flue gas sampling points with respect to the general layout of Crist No. 7. For more detail on the sampling system, refer to Figures 2-6 and 2-7. Flue gas was sampled downstream of the boilers economizer section and upstream of the air heater. This way, the sample represented combustion products rather than leaks from downstream components. At this location, the gas being sampled was about 500 to 800°F (260 to 467°C). Sampling tubes were assembled in four bunches of three and inserted vertically through ports on top of the two exhaust ducts. Each bundle of 3 sampling tubes is called a "probe" and consisted of a short, medium, and long tube.

The twelve sampling points were located as close as possible to the centers of twelve equal and mutually exclusive co-planar areas of the ducts' cross section. This method, though not in strict accord with EPA's method 1, has been shown to yield a representative sample (10).

For each probe, the 3 samples flowed through heated stainless steel lines into a heated gas mixing and conditioning box. In the box, particulate matter was filtered from each sample, while still hot and free of condensed moisture. The three flow rates were then equalized and combined. Upon leaving the heated box, the composite sample entered a permeation tube dryer where water was selectively removed from the sample.

Typically, the raw sample contained 10% water vapor mixed with particulate matter. The heated gas conditioning boxes first removed the particulate matter, and then the water, thus preventing the formation of "mud" in the sampling lines. Removal of water vapor allowed the sample to be subsequently cooled without fear of condensation which may have absorbed water soluble sample components such as NO_x, or in cold weather may have frozen and plugged the lines. With the water removed, the sample was allowed to cool to ambient temperature as it traveled under vacuum approximately 200 feet (61 m) through transluscent inert plastic tubing ("Polyflo" brand) to the pumping station.

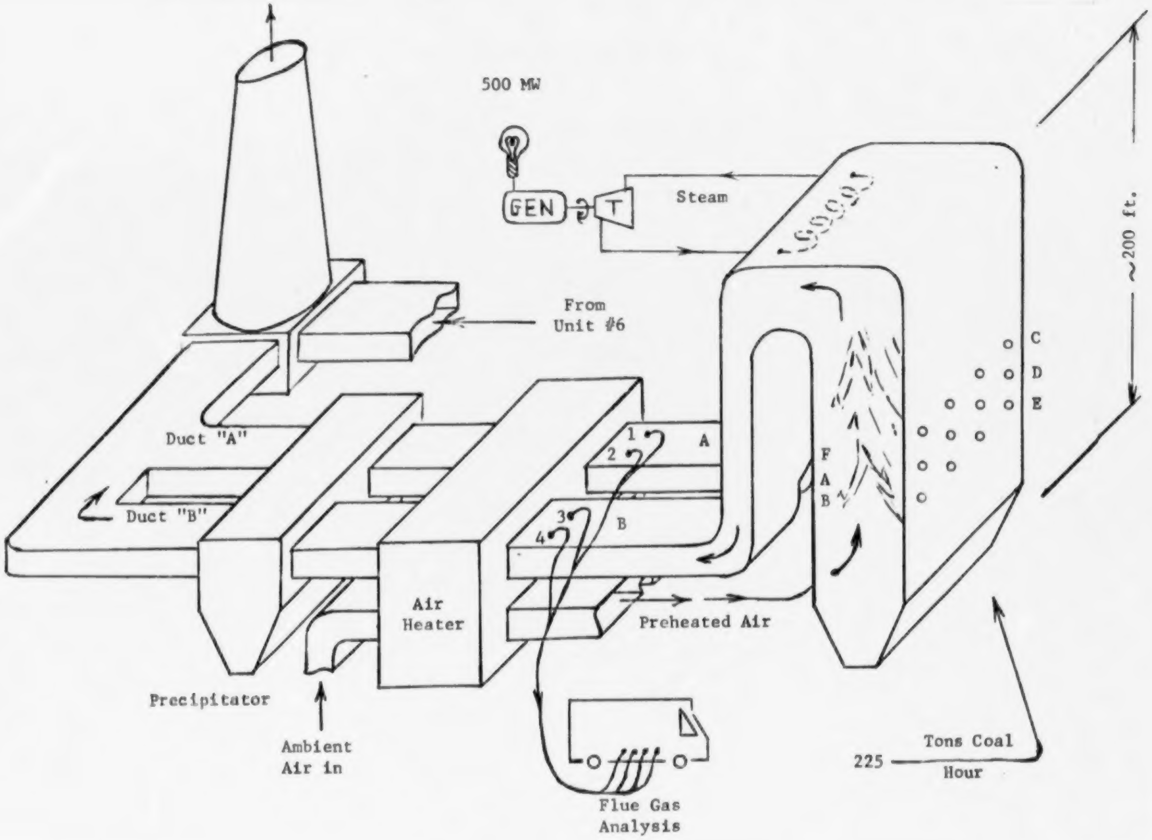

500 MW
GEN
T
Steam
From
Unit #6
~200 ft.
C
D
E
Duct "A"
Duct "B"
1
2
3
4
A
B
F
A
B
Air
Heater
Preheated Air
Precipitator
Ambient
Air in
Flue Gas
Analysis
225 Tons Coal / Hour

Figure 2-5. General layout and flue gas sampling points.

CRIST No. 7

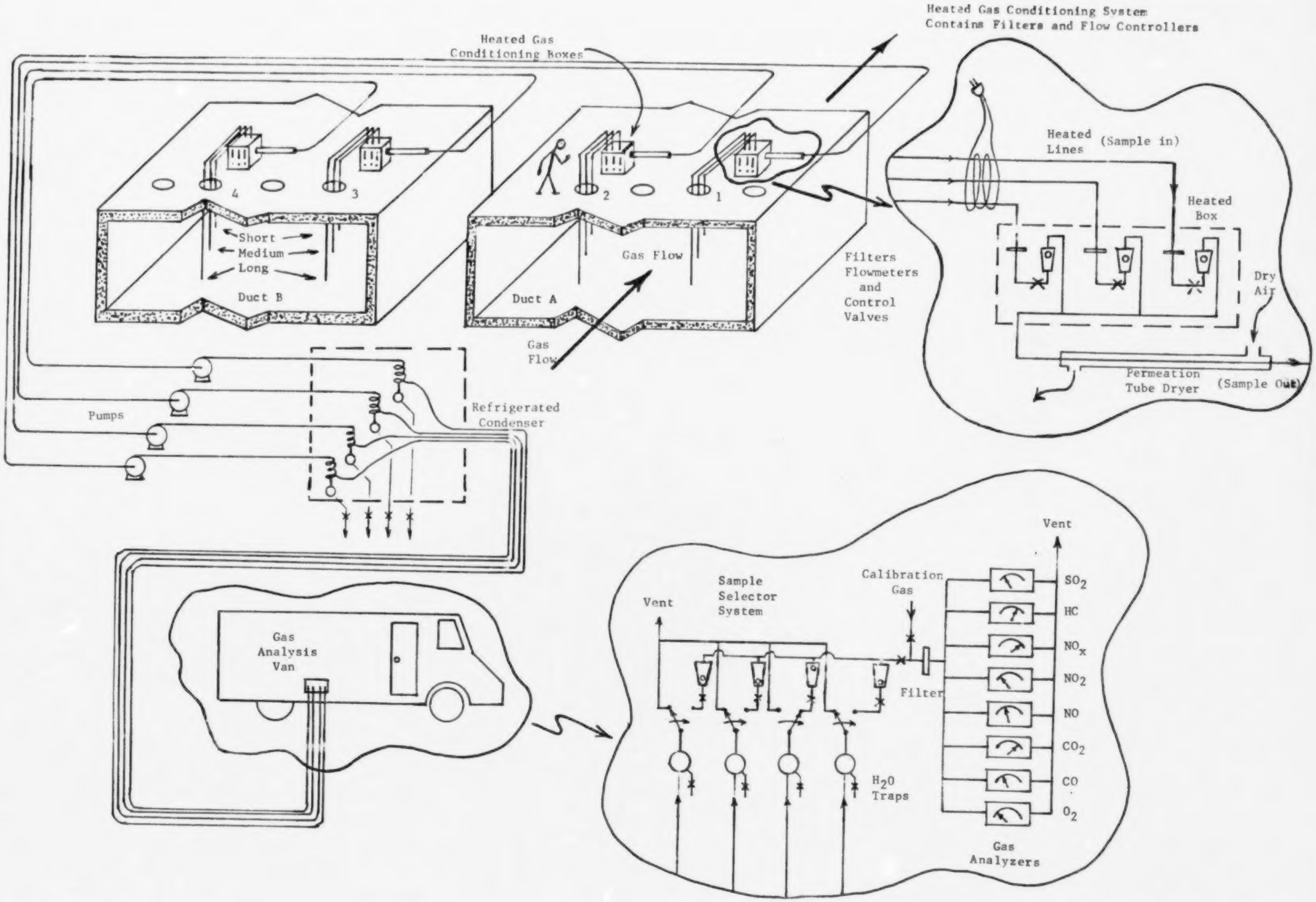
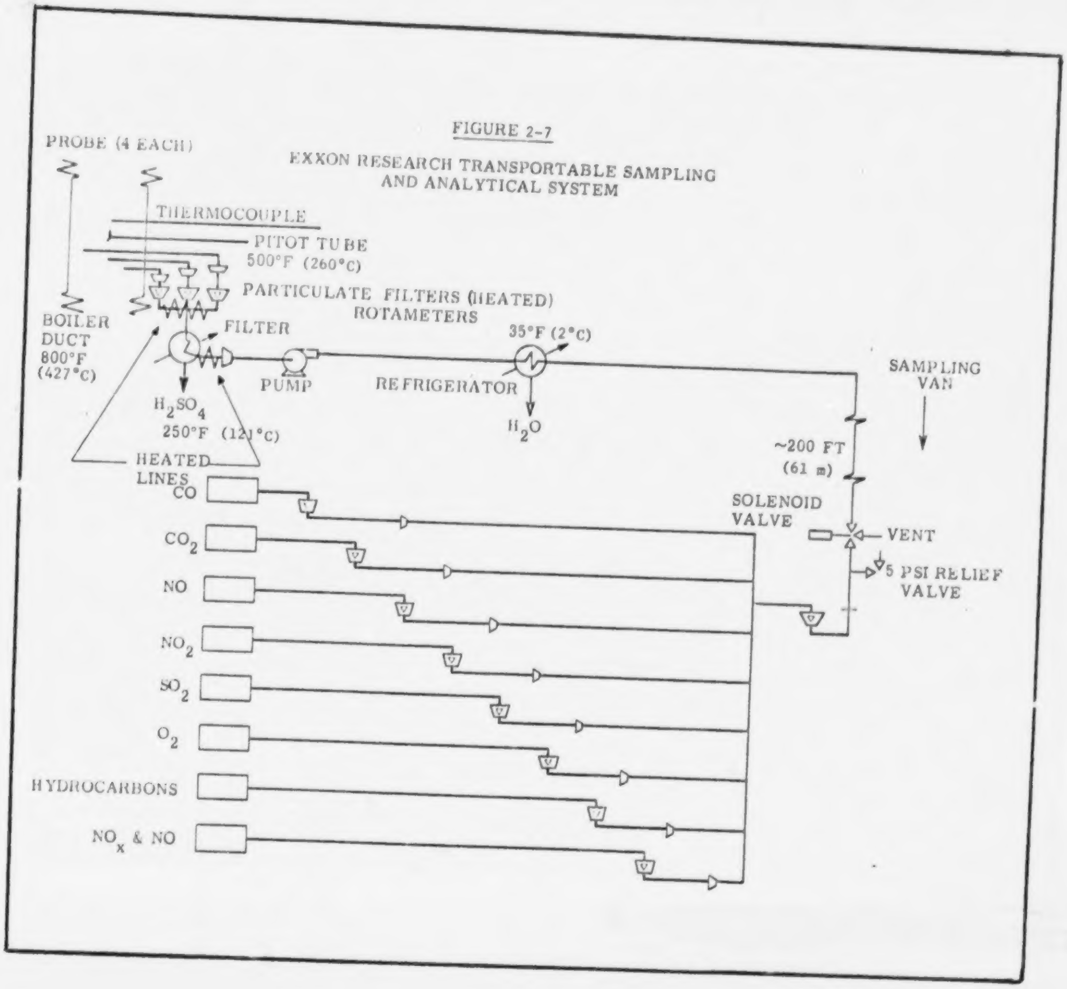

Heated Gas Conditioning System
Contains Filters and Flow Controllers
Heated Gas
Conditioning Boxes
4
3
2
1
Short
Medium
Long
Duct B
Duct A
Gas Flow
Gas
Flow
Filters
Flowmeters
and
Control
Valves
Heated
Lines
(Sample in)
Heated
Box
Dry
Air
Permeation
Tube Dryer
(Sample Out)
Pumps
Refrigerated
Condenser
Gas
Analysis
Van
Vent
Sample
Selector
System
Calibration
Gas
Filter
H_2O
Traps
Vent
SO_2
HC
NO_x
NO_2
NO
CO_2
CO
O_2
Gas
Analyzers

Figure 2-6. Gaseous sampling system.

FIGURE 2-7

EXXON RESEARCH TRANSPORTABLE SAMPLING AND ANALYTICAL SYSTEM


PROBE (4 EACH)
THERMOCOUPLE
PITOT TUBE
500°F (260°C)
PARTICULATE FILTERS (HEATED)
ROTAMETERS
BOILER DUCT
800°F
(427°C)
FILTER
H_2SO_4
250°F (121°C)
HEATED LINES
PUMP
35°F (2°C)
REFRIGERATOR
H_2O
SAMPLING VAN
~200 FT
(61 m)
SOLENOID VALVE
VENT
5 PSI RELIEF VALVE
CO
CO_2
NO
NO_2
SO_2
O_2
HYDROCARBONS
NO_x & NO

The sample entered the pump at a vacuum guage value of 15 in. (381 mm) Hg (51 kPa, draft) where it was pressurized to about 10 psig (69 kPa), and immediately entered a refrigerated coil where it was cooled to 35°F (2°C). The refrigerator removed the last traces of water. The dry (dew point <35°F (<2°C)) sample left the refrigerated condensation chamber still under pressure for its journey to the analytical instruments. These instruments were housed in a mobile laboratory. Eight of the analyzers used in the Crist test are shown schematically in Figure 2-7, and are summarized in Table 2-2.

As the gases entered the instrumented van they encountered a final water trap before entering the sample selection system. Here, the instrument operator selected one of the four composite samples to be distributed to the continuous gas analyzers. The other three were vented thus keeping each sample line filled and continuously purged with its own flowing sample all the way to the sample selector valves in the van. This minimized response time when switching sample lines.

Generally, only one sample (representing an equal composite of 3 sampling points), was monitored at a time. After about 2 minutes, the next composite sample was monitored, and so forth. For special tests, through use of the systems valves and flowmeters, a composite (in any ratio) of any one or more sample points could be mixed and fed to the instrument train. This was useful for leak checks, diagnostics, weighted averaging, calibration checks, and certain tests which required close monitoring of a critical sampling point or set of points.

The sample took approximately two minutes to travel from the sampling point to the instrument train.

(Other systems were used for SO_2-SO_3 and particulate sampling and analysis. These are discussed in Sections 2.7 and 2.5 respectively.)

Calibration was done by introducing "cal gas" at the gas analysis instrument. Leak checking was done by monitoring the sample's oxygen concentration. (A leak on the vacuum side of the pump would draw in air, causing the O_2 analyzer to show an unusually high reading.) In more recent tests, where calibration gas was introduced into the probe it was found that as long as the oxygen analyzer indicated no critical leaks, it did not matter whether calibration was done at the probe or at the gas analyzer.

The composition of the calibration gases is summarized on Table 2-3.

TABLE 2-2

MOBILE ANALYTICAL LABORATORY: CONTINUOUS GAS MONITORS AND CALIBRATION STANDARDS

Gas Monitored	Method	Manufacturer & Model	Measuring Ranges	Calibration Standard*
NO	non-dispersive infrared (NDIR)	Beckman	0-400 ppm 0-2000 ppm	3
NO_2	non-dispersive ultraviolet (NDUV)	Beckman	0-100 ppm 0-400 ppm	4
NO/NO_x	chemiluminescent	Thermo Electron 10 A	0-25 ppm 0-10 ppm 0-25 ppm 0-100 ppm 0-250 ppm 0-1000 ppm 0-2500 ppm 0-10000 ppm	3 & 4
O_2	polarographic	Teledyne	0-5% 0-25%	5 6
CO_2	non-dispersive infrared (NDIR)	Beckman	0-20%	2
CO	non-dispersive infrared (NDIR)	Beckman	0-200 ppm 0-1000 ppm 0-25000 ppm	2 1
SO_2	non-dispersive infrared (NDIR)	Beckman	0-600 ppm 0-3000 ppm	7
HC**	flame ionization detector (FID)	Beckman	0-10 ppm 0-100 ppm 0-1000 ppm	2

* See Table 2-3 for composition of calibration gas mixtures. In all cases nitrogen (mixture #8) was used for "zero" check.

**HC = Hydrocarbons (Since unheated sample lines were used, only volatile hydrocarbons could be sampled and delivered to the analyzer. Low boiling point hydrocarbons were lost in the sample lines.)

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TABLE 2-3

COMPOSITION OF STANDARD GAS MIXTURES USED FOR CALIBRATION OF GAS ANALYZERS (FOR USE WITH TABLE 2-2)

MIXTURE NUMBER	COMPONENTS	CONCENTRATIONS*
1	CO	15,000 PPM
2	CO CO_2 CH_4	150 PPM 13% 75 PPM
3	NO	500 PPM
4	NO_2	75 PPM
5	O_2	4%
6	Air	100%
7	SO_2	500 PPM
8	N_2	100%

In addition to the above, National Bureau of Standards (NBS) gases are kept and used as reference checks when accepting new calibration gases from suppliers. Each cylinder of calibration gas is checked against its NBS counterpart when possible.

*Nitrogen makes up the balance of all mixes.

2.4.2 Gaseous Sample at Furnace Wall

Another type of gaseous sampling which was routinely performed, involved extracting gases directly from various places along the walls of the combustion zone so that local potentially corrosive environments could be identified and selected for further study.

In preparation for the furnace gas tap study, approximately thirty, 1/4 inch (0.6 cm) holes were drilled through the furnace wall (in the membrane between adjacent tubes) during a boiler shutdown. A pipe (~3/8" (1 cm)) was welded over the hole so that a sample of furnace gas could be drawn through it from outside the boiler. Furnace gas tap locations are shown in Figure 2-2.

The sampling and analysis system used for these tests was essentially the same as was described in Section 2.4.1 of this report except that the line between the sample point and conditioning box was 200 feet (61 m) long rather than four feet (1.2 m) as was the case when the flue duct was sampled. This was because during the multi-point furnace gas tests, it was impractical to place a conditioning box close to each sampling port. Instead, only one box was used, and that box was left in place with one end of the sampling line attached to it. The other end of the long sampling line was carried and connected to each gas tap in turn. Because of the length of this line, it was impractical to heat it.

During a test, furnace gas was pulled, under vacuum, from the furnace and through a 10 to 20 foot (3 to 6 m), stainless steel coil where the gas was quickly quenched from its more than 2000°F (1093°C) reaction temperature to nearly ambient temperature. This quenching "froze" the reaction thus preserving for analysis the incompletely reacted species present at the sampling point.

From the coil, the sample flowed through about 200 feet (61 m) of 3/8" (1 cm) "Polyflo" brand plastic tubing to one of the 3 inlet ports on a gas conditioning box. (The other two ports were valved off.)

The remainder of the sampling and analysis train was the same as described in section 2.4.1 of this report.

When a furnace gas tap test was run, it was usually done shortly before or after, and in conjunction with, a flue duct test. This allowed comparison and correlation between emission data, operating mode, and furnace gas composition.

2.5 Particulate Sampling - Mass, Size Distribution

Particulate emissions in pulverized coal fired utility boilers are affected by the ash content and composition of the fired coal, coal fineness, burner design, type of firing and by burnout problems (increased carbon on particulates). Since no changes were made in pulverizer operation during the particulate tests conducted in the course of this contract, coal fineness was not a valid contributing factor to observed changes in particulate emissions. Combustion modification techniques used to control NO_x emissions, however, results in less intense combustion conditions than those corresponding to conventional firing methods and these techniques such as, lowering excess air levels, staging the combustion process and readjustment of burner dampers to decrease the air supplied to the flame zone can affect carbon burnout problems which may adversely affect particulate emissions. Lowering excess air tends to limit the amount of oxygen available for completion of the combustion process. This factor directionally increases the probability of burnout problems. Staging the combustion pattern, where the majority of the bottom burners are operated at substoichiometric air supply conditions and the remaining air is introduced either through inactive burners or overfire air ports to complete the combustion process, may have similar effects. Since staged combustion limits the amount of available oxygen in the burner zone, flames are lengthened, and turbulence is reduced, resulting in slower diffusive mixing of air and fuel. Thus, staged firing may also tend to increase unburned combustibles.

Beyond the issue of combustibles with potential changes in particulate mass loading, a further question to answer is whether particulate size distribution may be affected by low-NO_x operation of coal fired boilers. Part of the overall program plan, therefore, was to obtain information on the effect of combustion modifications on particulate mass loading and flyash particle size distribution. These measurements were made upstream* of the electrostatic precipitators in order to show the direct effect of the NO_x reduction techniques. Measurements of total mass loading and particle size distribution were made under both "baseline" and "low-NO_x" operating conditions to determine the extent of adverse effects of staged firing and other NO_x combustion modifications. Flyash was analyzed for unburned carbon content for use in these comparisons. Such information is needed to evaluate the impact of potential changes in particulates on electrostatic precipitator performance and to determine the effect of combustion modifications on trace species emission.

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*Concurrent with the Exxon work, Acurex Corp. conducted particulate sampling downstream of the precipitators as well as Level 1 testing under a separate contract to EPA (Contract # 68-02-2160).

Particulate emission tests were conducted using EPA Method 5, and SASS (see Section 2.8). The Method 5 type trains were modified to incorporate Brink, multistage cascade impactors (for particle size determination) in the heated oven between the cyclone and filter of the normal EPA train. A separate pump and flow rate measuring device was used to pull samples through the Brink impactor. This arrangement permitted simultaneous sampling for mass loading and particle size distribution determination at the required rates in isokinetic traverses of the boiler flue gas ducts with the Brink equipment located outside of the boiler. Thus, the proper recommended flow rates were obtained in the Brink impactor to obtain the specified aerodynamic diameter cut points. The Brink impactor consists of five stages, each having cut points (at rated conditions) at diameters of 2.5, 1.5, 1.0, 0.5 and 0.25 μm followed by a final filter. Combustion modifications for decreased NO_x emissions could change the particulate size distribution, and such a change in size distribution of flue gas particulates could affect electrostatic precipitator collection efficiency, especially if these changes occur in the smaller size (fine) fractions.

Generally, the tests were made in the boiler flue gas ducts downstream of the airheaters but upstream of any collecting devices, such as mechanical dust collectors or electrostatic precipitators. Consequently, the dust loadings are higher than at the outlet of the precipitator, but the results are not affected by the existing collection devices. Comparison of the test results taken under baseline operating conditions with data obtained under "low-NO_x" operation, therefore, provided a direct determination of potential side effects of NO_x reduction techniques on particulates.

In earlier ER&E field studies (7), some "side effects" attributed to "low-NO_x" firing were observed based on the fact that particulate mass loading in some boilers tended to increase, but not significantly, and the consequences appeared to be relatively minor. Results of later ER&E programs (8) also showed a tendency, in some cases, toward increased particulate emissions with "low-NO_x" firing but concluded that any increases or decreases in dust loadings observed did not appear to be significant. Measurements of those potential side effects were made during the course of these investigations and the results are discussed in Section 3.4.

2.6 Boiler Efficiency

Side effects of "low-NO_x" combustion modifications on boiler performance were investigated and evaluated for each major test. Control room board data and other pertinent information were recorded for baseline and optimum "low-NO_x" firing conditions and boiler efficiency was calculated in accordance with the ASME Steam Generating Units, Power Test Codes using the Abbreviated Efficiency Test, heat loss method. Calculations were based on the assumption that combustibles in the bottom ash slag were zero and unmeasured losses were 0.5 percent. Results are presented in Section 3.5.

Low-NO_x combustion modifications result in less intense combustion conditions. The effect is a tendency toward increased unburned combustibles which potentially may lower boiler efficiency. Differences in calculated boiler efficiency between baseline and "low-NO_x" tests help provide a comparison of adverse side effects due to "low-NO_x" firing. Such comparisons, however, may be made complicated by other factors affecting boiler efficiency such as load, differences in coal quality (Btu, moisture, ash content, etc.), carbon content of the particulate (combustible losses), etc. In general, efficiency increases with load and decreases with deterioration in coal quality (lower Btu, increased moisture and ash content, etc.) and increased combustible losses. Earlier ER&E field studies (7) indicated some increased combustible losses under "low-NO_x" combustion modifications but concluded that only negligible differences in boiler efficiency occurred due to this type of operation.

2.7 SO_2/SO_3 Gaseous Sampling

A modification of EPA Method No. 6 was used for wet chemical analysis of flue gas samples for sulfur oxides (SO_2 and SO_3) determination. Samples were taken from the boiler ducts at the same point where other gaseous emission samples were extracted for continuous analysis. Invariably this sampling point was located at the boiler outlet downstream of the economizer but upstream of the regenerative airheaters in order to eliminate dilution problems due to air leakage inherent in this type of airheater. Flue gas samples for sulfur oxides analysis were drawn from the ducts through a heated probe and passed through a series of absorbers. The first absorber, containing an 80% solution of isopropanol, absorbed the sulfur trioxide (SO_3) and the second, containing a 3% hydrogen peroxide solution, absorbed the sulfur dioxide (SO_2) as well as any SO_3 not absorbed by the first solution. The amounts absorbed were determined titrimetrically using barium perchlorate as the titrant for the SO_3 solution with thorin as an indicator. For the SO_2 solution, sodium hydroxide was the titrant and methyl-orange was the indicator.

It should be recognized that the sulfur dioxide content of the flue gases in any combustion installation is directly related to the sulfur content of the fuel burned. The sulfur trioxide content, however, may vary depending on operating conditions affecting the conversion of SO_2 to SO_3. Another factor affecting the quantity of sulfur oxides in the flue gases is the retention (or loss) of some of the sulfur within the combustion system. The ash content of the fuel and its chemical composition is also of great importance here. Sulfur oxide emission concentrations calculated on the assumption of 100% conversion of the sulfur content of the fuels burned are nearly always higher than measured sulfur oxides concentrations. This is not unexpected, especially in pulverized coal fired boilers. In the dry bottom pulverized coal fired boilers tested, 15 to 20 percent of the ash is extracted from the furnace as bottom ash and the remaining 80 to 85 percent is carried out of the boiler with the flue gases to electrostatic precipitators (or other collection devices) which collect 98 to 99 percent of the fly ash. Some of the fuel ash remains in the boiler as slag on the furnace walls or deposits in the convection sections and hoppers. A portion of the fuel sulfur content, in each case, may remain with these ash accumulations to decrease the total amount emitted as SO_2 or SO_3 in the flue gases. Only limited sulfur balance data are available but it may be expected that from 5 to 25 percent of the fuel sulfur may be retained in a boiler, especially where a boiler is fired with a high calcium content coal.

2.8 SASS Train Sampling of Stack Emissions

In cooperative tests with the Acurex Corp. combustion products from the No. 7 boiler at Gulf Power Company's Crist Station were sampled by ER&E at the inlet to the electrostatic precipitator (ESP) during June 1978 using a Source Assessment Sampling System (SASS train sampler) developed by EPA (IERL-RTP) and manufactured by Acurex Aerotherm Corporation. Concurrent with each ER&E SASS test at the ESP inlet, Acurex, under a separate EPA contract (reported separately), performed a SASS test at the ESP outlet. Four such inlet-outlet test pairs were performed. However, only test pair Nos. 3 and 4 were analyzed completely. Acurex was responsible for the analysis of both the outlet as well as the inlet samples. This report contains the inlet results. This work was part of a "Level 1" test involving sampling by SASS as well as sampling for total particulate loading and size distribution in the flue gas stream by Method 5 and Brink impactors, respectively.

During these tests, flue gas was monitored as usual between the economizer and air heater. The main purpose of these tests was to determine the extent of toxic materials emitted to the atmosphere by this pulverized-coal-fired boiler and whether the magnitude of the emissions might be different when the boiler was operated under low-NO_x combustion modification conditions. Two tests analyzed were; one at baseline conditions performed on June 22, 1978 (test 3), and the other (test 4) under low-NO_x firing conditions; samples acquired on June 23, 1978. (These correspond, respectively, with flue gas tests 152 and 153 which are discussed in Sections 3.1 and 4.1 of this report.) Analysis of the samples was performed by the Acurex Corporation. The analytical methodology is discussed in the following pages, and details of the analytical techniques used in screening for toxic materials are covered in Appendix E. Details of the sampling system employed in obtaining the stack samples are also described below.

2.8.1 Analytical Methodology

Level 1 analyses were performed as described in the first edition of the IERL-RTP Procedures Manual for Level 1 Environmental Assessment (ref. No. 12) and amended by Acurex Corporation (see Figure E-1 in Appendix E). Elemental analyses of twenty-four elements were done by atomic absorption. Corrections for blanks and matrix interferences were made. Boron was analyzed by the curcumin method. Leachable ions were determined by classical wet chemical and selective ion electrode techniques. Organic analyses were performed on the combined total particulate catch and XAD-2 resin plus extracted condensate.

2.8.2 Sampling and Analysis

Some particulate samples were collected with a SASS train. The main objective was to have a single device which would sample stack emissions for particulate and organic materials simultaneously. A diagram detailing the various components of the system is illustrated in Figure 2-8.

The flue gases first pass through a heated stainless steel probe and then into an oven which is maintained at 400°F (204°C). In this oven there are three cyclones which are used to separate particles by size (10 μm, 3 μm, 1 μm) prior to the entrapment of material less than 1 μm on a final filter. The hot gases are then cooled to approximately 70°F (21°C). The resulting condensate and remaining gases pass through an XAD-2 adsorbent catridge. The purpose of the XAD-2 resin is to adsorb organic materials which are present either in the liquid or gaseous form. The organic materials of main interest are PNA's (polynuclear aromatic hydrocarbons). The condensate solution which has passed through the XAD-2 resin bed then drains into a trap. Depending on the amount of condensate collected over a typical run time (~5 hr), the liquid is periodically removed from the trap.

The impinger solutions serve a three-fold purpose. The first impinger, which contains hydrogen peroxide, prevents reducing gases such as sulfur dioxide from reducing the collection efficiency of impingers 2 and 3. These impingers contain ammonium persulfate and silver nitrate dissolution. A fourth impinger which contains silica gel is used to prevent moisture from reaching the SASS train pumps.

Sample is typically collected at a rate of 4.0 standard ft^3/min (SCFM) (1.9 dm^3/S). At this rate almost 5 hours of continuous operation are required to collect the desired 30 m^3 (~ 1,000 scf) of sample. Gas volumes sampled during each test run are listed in Table 3-58 (footnote b), in Section 3 of this report.

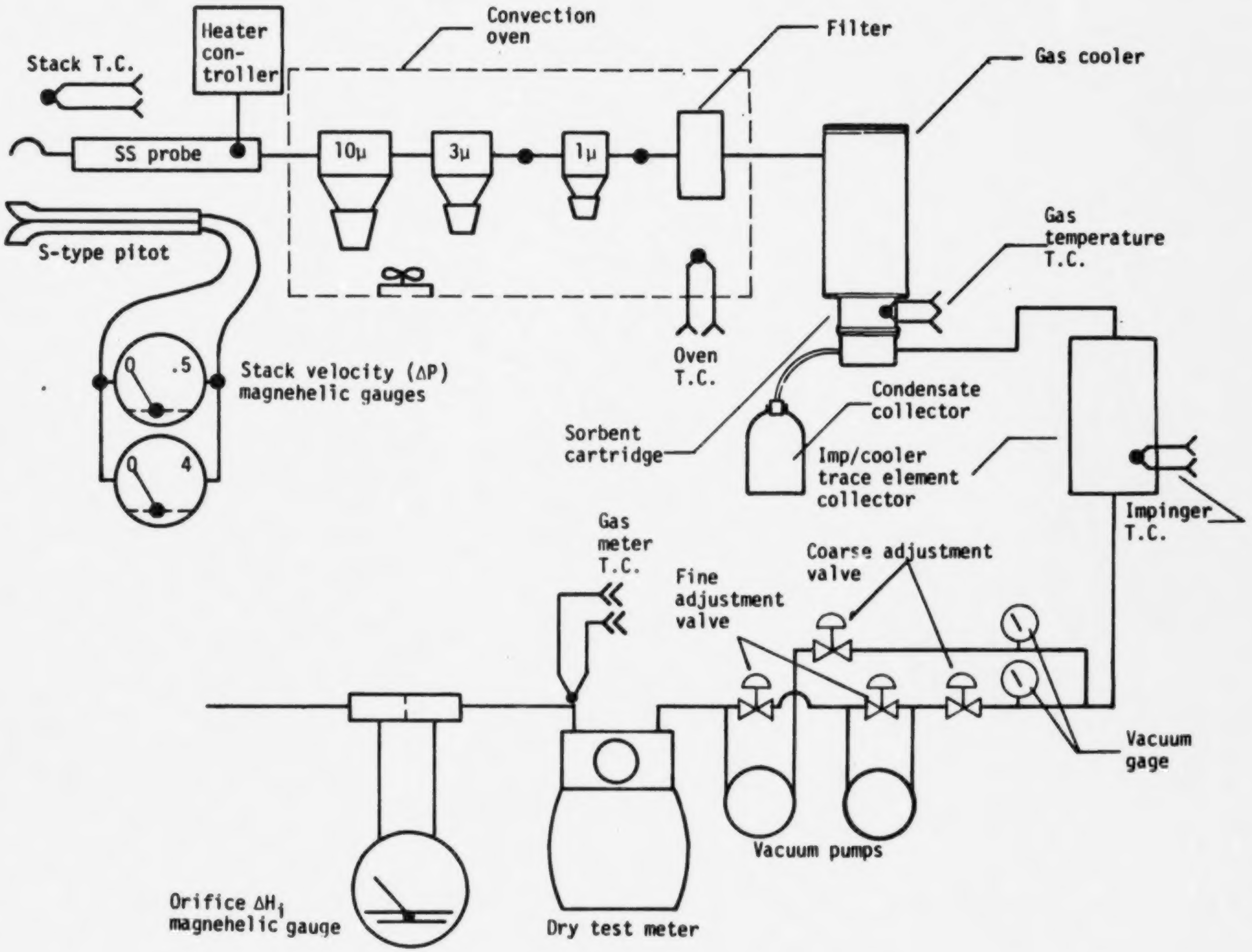
Stack T.C.
Heater con-troller
Convection oven
Filter
Gas cooler
SS probe
10μ
3μ
1μ
S-type pitot
Gas temperature T.C.
.5
4
Stack velocity (ΔP) magnehelic gauges
Oven T.C.
Condensate collector
Sorbent cartridge
Imp/cooler trace element collector
Impinger T.C.
Gas meter T.C.
Coarse adjustment valve
Fine adjustment valve
Vacuum gage
Vacuum pumps
Orifice ΔH_i magnehelic gauge
Dry test meter

Figure 2-8. Schematic of SASS.(11)

3. RESULTS AND DISCUSSION

Test conditions and controls investigated are described on Table 3-1. The table is a matrix of test numbers, sorted and grouped according to boiler operating conditions during the respective tests. The table provides information for identifying similar tests and will be referenced in the following discussion. Note that the most frequently tested condition was at full load, with normal air flow, using firing mode #5, and register configuration "B." These terms are explained in sections 3.1.1 through 3.1.4 of this report.

Parameters indicating boiler operating conditions (control room board data) were recorded each time a flue gas analysis test was performed. But, besides flue gas tests, a variety of other test were also performed on Crist No. 7. These included:

- o Furnace gas analysis tests
- o corrosion probe tests
- o particulate loading tests
- o particulate size distribution tests
- o precipitator efficiency tests
- o boiler efficiency tests
- o SO_2-SO_3 tests for sulfur balance analysis
- o coal analysis tests
- o Level 1 tests for screening other emissions

Generally each of the above tests was associated (performed concurrently) with a flue-gas analysis test. In most cases, these associated tests shared the same test number as the corresponding flue gas test. Table 3-2 lists all flue gas tests as well as some of the other associated tests performed in the same time period (under the same conditions) as each flue gas test.

3.1 Gaseous Emission Results (NO_x, CO, HC, SO_2) and Investigated NO_x Control Methods

Flue gas analysis focused mostly on NO_x emissions, however the response of other emissions to various boiler combustion modification controls was also measured.

Two separte mechanisms are responsible for NO_x emissions from coal-fired boilers. "Fuel NO_x" is formed when the nitrogen bound in the fuel is released during excess-air combustion. The atomic nitrogen bound to hydrocarbon molecules is released as the hydrocarbon is consumed. The higher the oxygen concentration in the flame (a result of both excess air and mixing) the higher will be the NO_x emission. With pre-NSPS turbulent burners, such as the Crist No. 7 burners, fuel/air mixing is rapid and results in a short, intense flame. Starving the flame of oxygen in its early stages of combustion will favor the production of N_2 (rather than NO) as an intermediate combustion product. Subsequently, the remainder of the air necessary for complete combustion may be added. This mixing control, or staging of the furnace

TABLE 3-1

FLUE GAS TESTS
(TEST NUMBERS GROUPED BY TEST CONDITIONS)

——— Expected Best for Low NO_x ———→

Expected Best for Low NO_x ↓

Load	Firing Pattern	Secondary Air Register (Burner Damper) Configuration (Top-Middle-Bottom)							
		A (33-33-33)		B (40-30-30)		C (55-25-20)		D (60-25-15)	
		Normal Air	Low Air	Normal Air	Low Air	Normal Air	Low Air	Normal Air	Low Air
High - Full (440-510 MW)	3			128					
	4							73*	
	5	1, 1A, 122, 122A	2, 2A	3, 1B, 1C, 3A, 1E*, 202, 201*, 205, 206, 100B*, 123, 125*, 126*, 129	4, 4A 204A*, 204B*,	100, 124	101	71*, 72, 81, 82	80
	6	31							
	7	59*, 60*, 61*							
	11			7	8, 4C*, 4D*, 4E*, 137*			83, 84B	85
Reduced (350-450 MW)	4			203, 204				78*	
	5			1D, 150* 152, 200*		104	105		
	7	56, 57		127, 131, 132					
	8		58						
	9							74	
	10							69*	
	11			7A	8A	91*, 93	92, 94 102	98, 103	95
	12			32					
	13	63	64	11, 11A, 11B, 11C	12, 12A	106	89, 90, 107	65*, 66*, 67*	151* 153*
Low-Medium (150-350 MW)	1			23	24*			88*	
	2	55		150					
	5			135					
	8	53		33					
	9							75*, 76*, 77*, 79*	
	13	62		133*	134*, 136*			86, 87	
	14							68*	
	15			17, 17A	18, 18A	117	118		
	16			34					
	17	50, 51, 52							
	18	54*							

*See notes on next page.

*See Notes

FOOTNOTES FOR TABLE 3-1 (PG 1 of 2)

FLUE GAS TESTS
(TEST NUMBERS GROUPED BY TEST CONDITIONS)

Test Number	Note
1F, 4C, 4D, 4E	On each test in this sequence, the coal feed to Burner Rows C&F was reduced.
24	Low reheat temperature prevented lower air flow.
54	Two burners in D row are firing gas.
59-61	Burners B-21 and E-11 are out.
61	Burners B-21 and E-11 are out. Damper B-21 open 10%, damper E-11 open 28%
65-69	1 burner in B row, and 2 in E row are off.
69	C row fuel-lean, F row fuel-rich.
71	3 burners off.
73	E row off. 2 burners with dampers closed, 2 open 30%.
75-77	E has two burners on air only.
76	Higher air flow than normal.
78, 79	E row has 2 burners on air, B has 1 on air.
88	Air register settings are somewhat uncertain, may have been set at configuration "C" (date uncertain).
91	Air flow higher than normal.
100B	Air register setting are somewhat uncertain.
125	Registers were reset during this test.
126	B mill went down after duct taps were completed, but furnace taps still being sampled.
131	Load was upset during this test and then returned to initial condition.
133, 134, 136	One top mill off. Other fuel lean.
137	This is a test of Exxon's table of guidelines for Crist #7 operators. The table gives optimum operating conditions for low NO_x based on tests done to date.

FOOTNOTES FOR TABLE 3-1 (PG 2 of 2)

Test Number	Note
150-153	Level one tests.
200	Furnace gas taps started at 500 MW. Load reduced to 400 MW during furnace gas taps. Flue-gas analyzed after furnace-gas test.
204A, 204B	Low NO_x particulate test with Entropy.
204B	No van data.

TABLE 3-2

TEST AND DATE CROSS REFERENCE TABLE - PART I (BY TEST NUMBER)
(TEST NUMBERS & DATES PERFORMED)

-- In Order By Test Number --

Flue Gas Analyses								Furnace Gas Analysis	
Test	Date	Test	Date	Test	Date	Test	Date	Test	Date
1	3/1/76	31	3/1/76	77	1/12/77	107	1/23/78	52A	11/05/76
1A	3/2/76	32	3/12/76	78	1/13/77	117	1/23/78	53A	11/12/76
1B	3/3/76	33	3/15/76	79	1/13/77	118	1/23/78	55A	11/16/76
1C	3/8/76	34	3/16/76	80(5)	1/17/77	122	1/18/78	56A	12/02/76
1D	3/11/76	50	11/3/76	81	1/21/77	122A	1/19/78	57A	12/7/76
1E	4/6/76	51	11/4/76	82	1/24/77	123	1/27/78	59A	12/13/76
1F(1)	4/8/76	52	11/05/80	83	1/24/77	124	1/27/78	61A	12/14/76
1G (1)	4/8/76	53	11/12/76	84(4)	1/24/77	125	2/2/78	79A	1/13/77
2	3/1/76	54	11/15/76	84A(4)	1/24/77	126	2/3/78	88A	1/27/77
2A	3/1/76	55	11/16/76	84B(7)	1/25/77	127	2/7/78	89B	1/28/77
3	3/2/76	56	12/2/76	85	1/25/77	128	2/7/78	91A	1/31/77
3A	3/23/76	56B	12/2/76	86	1/26/77	129	2/8/78	93A	2/1/77
4	3/2/76	57	12/7/76	87	1/27/77	130	2/9/78	94A	2/1/77
4A(5)	3/24/76	58	12/8/76	88(5)	1/26/77	131	2/15/78	96A	2/2/77
4C	4/6/76	58B	12/8/76	89	1/28/77	132	2/16/78	125	2/2/78
4D	4/7/76	59	12/13/76	89A	1/28/77	133	2/22/78	126	2/3/78
4E	4/7/76	60	12/14/76	90	1/28/77	134	2/22/78	130	2/10/78
7	3/2/76	61	12/14/76	91	1/31/77	135	3/1/78	132	2/16/78
7A	3/8/76	62	12/15/76	92	1/31/77	136	3/1/78	134	2/23/78
8	3/3/76	63	1/4/77	93	2/1/77	137	3/2/78	136	3/2/78
8A	3/8/76	64	1/4/77	94	2/1/77	150(2)	6/20/78	137	3/2/78
11	3/3/76	65	1/6/77	95	2/1/77	151(2)	6/21/78	200	6/11/76
11A	3/8/76	66	1/6/77	96(4)	2/2/77	152(2,8)	6/22/78		
11B	3/9/76	67	1/6/77	97	2/2/77	153(2,8)	6/23/78		
11C	3/12/76	68	1/6/77	98	2/2/77	200	6/11/76		
12	3/3/76	69	1/10/77	100	1/18/78	201	6/16/76		
12A	3/9/76	70(6)	1/10/77	100B	1/19/78	202	6/17/76		
17	3/15/76	71	1/11/77	101	1/18/78	203	6/28/76		
17A	3/16/76	72(6)	1/12/77	102	1/23/78	204	6/28/76		
18	3/15/76	73	1/12/77	103	1/23/78	204A(2)	3/30/76		
18A	3/16/76	74	1/12/77	104	1/23/78	204B(2,3)	4/1/76		
23	3/4/76	75	1/12/77	105	1/23/78	205	6/29/76		
24	3/5/76	76	1/12/77	106	1/23/78	206	6/29/76		

Notes:

(1) SO_2-SO_3 test performed concurrently.
(2) Particulate test performed concurrently.
(3) No van data.
(4) No board data.
(5) Date is not certain
(6) Test aborted.
(7) Test ID number not certain.
(8) SASS Test performed concurrently.

(Continued)

TABLE 3-2 (CONT'D)

TEST AND DATE CROSS REFERENCE TABLE - PART II (BY DATE)
(TEST NUMBERS & DATES PERFORMED)

In Order by Date

Date	Test Number (Flue Gas Analyses)**	Test Number (Furnace Gas Analyses)**
3/1/76	1, 2, 2A, 31	
3/2/76	1A, 3, 4, 7	
3/3/76	1B, 8, 11, 12	
3/4/76	23	
3/5/76	24	
3/8/76	7A, 8A, 11A, 1C	
3/9/76	11B, 12A	
3/11/76	1D	
3/12/76	11C, 32	
3/15/76	17, 18, 33	
3/16/76	17A, 18A, 34	
3/23/76	3A	
3/24/76	4A	
3/30/76	204A	
4/1/76	204B	
4/6/76	1E, 4C	
4/7/76	4D, 4E	
4/8/76	1F, 1G	
6/11/76	200	200
6/16/76	201	
6/17/76	202	
6/28/76	203, 204	
6/29/76	205, 206	
11/3/76	50	
11/4/76	82	
11/5/76	52	52A
11/12/76	53	53A
11/15/76	54	
11/16/76	55	55A
12/2/76	56, 56B	56A
12/7/76	57	57A
12/8/76	58, 58B	
12/13/76	59	
12/14/76	60, 61	61A
12/15/76	62	
1/4/77	63, 64	
1/6/77	65, 66, 67, 68	
1/10/77	69, 70	
1/11/77	71	
1/12/77	72, 73, 74, 75; 76, 77	
1/13/77	78, 79	79A
1/17/77	80	
1/21/77	81	
1/24/77	82, 83, 84, 84A	
1/25/77	84B, 85	
1/26/77	86, 87	
1/27/77	88	88A
1/28/77	89, 89A, 90	89B
1/31/77	91, 92	91A
2/1/77	93, 94, 95	93A, 94A
2/2/77	96, 97, 98	96A
1/18/78	122, 100, 101	
1/19/78	100B, 122A	
1/23/78	102, 103, 104,.105, 106, 107, 117, 118	
1/27/78	123, 124	
2/2/78	125	125
2/3/78	126	126
2/7/78	127, 128	
2/8/78	129	
2/9/78	130 (11 PM)	
2/10/78		130 (1 AM)*
2/15/78	131	
2/16/78	132	132
2/22/78	133, 134 (11 PM)*	
2/23/78		134 (1 AM)*
3/1/78	135, 136 (11 PM)*	
3/2/78	137	136 (1 AM)*, 137
6/20/78	150	
6/21/78	151	
6/22/78	152	
6/23/78	153	

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*Numbers in parenthesis indicate starting time for tests performed close to midnight.
**For list of other concurrent tests, see footnotes on Part I of this table.

Note: Footnotes concerning type of testing performed are on Part I of this table.

yields significant reductions in fuel NO_x emissions. Fuel NO_x is affected by coal rank and oxygen content, but is not as sensitive to flame-temperature changes as is thermal-NO_x.

"Thermal-NO_x" results from the high temperature reaction of the nitrogen and oxygen brought in with the air used to sustain combustion. Its abatement is achieved through those combustion controls which cause lower flame temperatures, or decreased availability of reactants (air). Flame temperature can be decreased by using "Low-NO_x" diffusion burners to stretch out the flame, causing it to be long and lazy thus giving off its heat over a longer time and distance. Reducing excess air to the design value (about 18%) will further improve the NO_x situation. Modern low-NO_x burners reduce fuel NO_x by controlling the mixing rate between the fuel and combustion air and also reduce thermal-NO_x by depressing the flame temperature.

The types of combustion modifications which result in lower flame temperatures (without specifically citing low-NO_x burners) include:

- Increasing the physical size of the furnace to provide more heat transfer surface. This type of modification is not feasible as a retrofit. (Derating the boiler is another way to increase the surface area to load ratio.)

- Increasing the time required for combustion. The fuel can be caused to burn more slowly by decreasing the air feed rate, or by adding the air in stages along the path of the combustion gases. Such "staging" results in a longer (and cooler) flame.

- Flue gas recirculation (FGR) will depress flame temperatures, but its utility is decreased if other NO_x controls are already in use. Also, though effective on thermal NO_x, FGR has little effect on fuel NO_x.

At Crist No. 7 four methods of combustion modification (CM) for NO_x control were studied. During the CM tests for NO_x control, each of four boiler operating parameters were independently varied and the effect of each on NO_x emissions was measured. These parameters were:

1) Secondary air biasing (attempted to vary the air distribution by adjusting the secondary air registers)
2) Firing pattern (biasing the fuel distribution to the burners)
3) Load (boiler's steam flow is reflected in generator electric output)
4) Boiler excess air

This section presents results of the tests designed to evaluate these various boiler combustion controls, and especially their effect on NO_x emissions. (Comments and discussion may be found in Section 4.1.) Any one of the four boiler operating parameters used for NO_x control may be evaluated by holding the other 3 constant while the one of interest is changed. This scheme will now be used to evaluate all four of the parameters investigated for NO_x control.

3.1.1 Effect of Secondary Air Register Settings on NO_x Emissions

The primary function of the secondary air register is to induce a controlled amount of swirl to the secondary air flow. This provides for flame stabilization and flame shape control. Although registers may be biased or unbalanced to some extent to adjust air distribution between the burners, FW has explained that this is only a secondary function of the registers. Flame shapes are adjusted for optimum stability, turndown, and correct radiant heat transfer in the burner zone. It is therefore preferable to use a separate damper system to control air distribution independently from air swirl. This type of system is incorporated into the low-NO_x burners of at least one boiler manufacturer. In this program, an attempt was made to use the registers to control the distribution of the air (needed to burn the fuel) among the boiler's 24 burners (Figure 2-2).

Each burner has its own register. "Secondary" air makes up more than 75% of the total air entering the boiler. The other ∿ 25% is "primary" air and is used to blow the coal fuel into the boiler. Primary air flow depends on the coal feed rate, and cannot be independently varied. The secondary air, however, can be varied to some extent through use of the secondary-air registers found on each burner.

The secondary air registers' automatic control system was not used during the test period. Instead, the dampers were set manually and left at the selected setting. Hence, for any burner, even if its fuel were shut off, air would continue to flow to it through its secondary air system, just as if it were burning fuel.

Each register "set-up" (consisting of 24 individual register damper settings; one for each burner) was called a "register configuration." Approximately 20 configurations were tested. However, during the analysis of these tests, many configurations were calculated* to be approximately equivalent. Finally, four (A, B, C, D) truly unique configurations were identified. Each of the 20 configurations tested was reassigned a configuration identification of either A, B, C, or D, as described in the following paragraphs.

A complete description of all 20 configurations may be found in Table 3-3. The 20 configurations have been sorted into four types (A,B,C,D) as described in Table 3-4. The designation of the four types was chosen such that with equal total air flows, configuration A distributes the least air to the upper

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*The calculation method was a modification of a damper flow method presented in an EPA publication (13) related to tangentially fired boilers.

TABLE 3-3

HISTORY OF SECONDARY-AIR-DAMPER SETTINGS (PERCENT OPEN)

Configuration (See Comments Below)	Top Level											Middle Level											Bottom Level										
	Front Wall					Rear Wall					Front And Rear	Front Wall					Rear Wall					Front And Rear	Front Wall					Rear Wall					Front And Rear
	Each Burner				Avg.	Each Burner				Avg.	Avg.	Each burner				Avg.	Each burner				Avg.	Avg.	Each Burner				Avg.	Each Burner				Avg.	Avg.
	C1	C2	C3	C4	C	F13	F14	F15	F16	F	C&F	D5	D6	D7	D8	D	A17	A18	A19	A20	A	D&A	E9	E10	E11	E12	E	B21	B22	B23	B24	B	E&B
1	48	92	82	68	72	75	32	42	55	51	62	57	100	78	88	79	40	52	55	50	49	64	65	66	63	62	64	38	48	62	100	62	63
2	53	92	72	73	72	75	32	48	65	55	64	45	92	70	88	74	40	40	40	40	40	57	52	53	55	56	54	38	40	58	65	50	52
3	20	100	60	90	67	-	70	50	100	73	70	30	(0?)	60	50	47	40	50	60	50	50	49	80	80	70	40	67	40	30	80	-	50	59
4	100	100	100	60	90	70	80	100	100	87	89	40	60	90	100	72	90	100	90	80	90	81	10	100	60	60	57	80	100	100	100	95	76
5	80	79	79	44	70	-	80	80	73	78	74	40	40	40	41	40	47	40	88	45	55	47	45	40	22	38	36	0	40	49	-	30	33
6	80	80	79	48	72	-	80	80	73	78	75	40	40	40	41	40	47	40	88	45	55	47	60	50	42	50	51	49	40	34	-	41	46
7	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50
8	60	60	79	50	62	80	80	50	80	72	67	50	40	40	51	45	40	40	40	40	40	42	40	40	39	49	42	35	40	40	40	39	40
9	60	60	79	50	62	80	80	50	80	72	67	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	~50	50
10	66	60	50	50	55	50	50	50	50	50	52	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
11	60	60	80	63	66	80	80	50	80	72	69	50	40	40	50	45	40	40	40	40	40	42	40	40	40	43	41	40	40	40	40	40	40
12	52	63	60	60	59	55	56	50	60	55	57	50	40	40	51	45	40	50	40	50	45	45	40	40	40	45	41	40	40	40	50	42	41
13	55	65	80	60	65	80	80	50	80	72	69	50	40	40	51	45	40	50	40	50	45	45	40	40	40	45	41	40	40	40	50	42	41
14	55	60	60	60	59	60	60	52	60	58	59	50	50	42	52	48	40	50	50	50	58	47	50	45	48	55	51	40	40	50	50	45	48
15	55	60	60	60	59	60	60	52	60	58	59	50	40	40	52	46	40	40	40	40	40	43	40	40	40	40	40	40	40	40	40	40	40
16	80	100	73	90	86	70	45	100?	65	70	78	53	55	45	50	51	30	50	65	60	51	51	50	80	50	60	60	50?	60	60	60	58	59
17	100	100	75	98	91	65	50	100?	60	69	80	50	53	45	50?	50	30	50	65	60	51	50	50	80	50	60	60	50?	60	60	60	58	59
18	100	100	80	98	96	100	80	100	70	87	91	50	43	40	50	46	40	40	40	45	41	43	40	45	40	50	44	50	45	50	50	49	46
19	80	82	80	80	80	65	70	100	70	76	78	60	60	60	50	57	40	57	60	60	54	56	55	60	60	60	58	50	60	60	60	57	57
20	100	100	80	98	95	100	100	100	85	96	95	50	40	40	50	45	40	40	40	40	40	43	40	40	40	50	42	45	45	42	50	45	43

COMMENTS

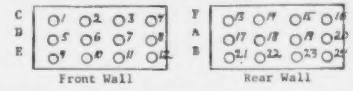
Configuration (See Above)	Dates in Effect: From	Dates in Effect: To	Test Involved	Attempted Damper Setting T	Attempted Damper Setting M	Attempted Damper Setting B	Actual Damper Setting T	Actual Damper Setting M	Actual Damper Setting B
1	<3-2-76	3-2-76	31, 1, 2, 2A, 1A	As Found			62	64	63(1)
2	3-2-76	<6-16-76	4, 3, 7, 1B, 11, 12, 23. 24, 11A, 7A, 8A. 1C 11B, 12A, 1D, 32. 11C. 33, 17, 18. 34, 17A, 18A, 3A, 4A, 204A, 204B, 1E, 4C, 4D, 4E	70	40	40	64	57	52
3	<6-16-76	<10-20-76	200, 201, 202, 203, 204, 205, 206	As Found			70	49	59
4	10-20-76	<1-5-77	50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64	80	40	40	89	81	76
5	<1-5-77	1-27-77	65-79, 79A, 80-84, 84A, 84B, 85-87, 88,(8) 88A(8)	80	40	40	74	47	33
6	1-27-77	<1-27-77	89, 89A, 89B, 90, 91, 91A, 92, 93, 93A, 94 94A, 95, 96, 96A, 97, 98	80	40	40	75	47	46
7	>1-27-77	≤1-18-78	122	50	50	50	~50	~50	~50(2)
8	1-18-78	~1-18-78	100, 101	80	40	40	67	42	40
9	1-18-78	1-19-78	100B	As Plant Desired			67	50	50(3)
10	1-20-78	1-23-78	122A	50	50	50	52	50	50
11	1-23-78	1-25-78	117, 118, 102, 103, 104, 105, 106, 107	70	40	40	69	42	40
12	1-25-78	1-27-78	123	60	40	40	57	45	41(4)
13	1-27-78	2-2-78	124	80	40	40	69	45	41
14	2-2-78	2-2-78	125	60	40	40	59	47	48(5)
15	2-2-78	<6-7-78	126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137	60	40	40	59	43	40
16	~6-7-78	6-20-78		As Plant Set Them			76	51	59(6)
17	<6-20-78	6-21-78	150	~As Found			80	50	59(7)
18	6-21-78	6-22-78	151	~100	~50	~50	91	43	46(7)
19	6-22-78	6-23-78	152	~ 80	~60	~60	98	56	57(7)
20	6-23-78	6-23-78	153	~ 95	~45	~45	95	43	43(7)

Notes:

(1) As Found: typical pretest condition.
(2) Typical pretest condition.
(3) This condition was set up without Exxon's knowledge.
(4) As plant would like to run.
(5) Reset during test #125.
(6) No test done here.
(7) Level 1 Tests.
(8) Exact time of change is uncertain. Tests 88, and 88A, may belong under Configuration #6.

T = Top (C&F)
M = Middle (D&A)
B = Bottom (E&B)

Many registers are broken, or jammed and hence could not be set as desired.



Elevation view of burner zone as seen from outside the boiler.

TABLE 3-4

SECONDARY AIR DAMPER CONFIGURATIONS

Configuration Number (From Table 3-3)	Equivalent Configuration Type
1	A
2	B
3	B
4	A
5	D
6	C
7	A
8	C
9	B
10	A
11	C
12	B
13	C
14	B
15	B
16	B
17	B
18	D
19	B
20	D

TABLE 3-5

SECONDARY AIR DISTRIBUTION VS. SECONDARY AIR DAMPER CONFIGURATION

Damper Configuration	Percent of Total Secondary Air Entering Boiler at each Burner Elevation			
	Top (C&F)	Middle (A&D)	Bottom (B&E)	Total Top, Middle and Bottom
A	33	33	33	100
B	40	30	30	100
C	55	25	20	100
D	60	25	15	100

burners, and D, the most. The relative distribution of total air for each of the four register configurations is shown in Table 3-5.

Test results show that NO_x emissions decrease as a greater proportion of air is introduced to the top burners, and less at the bottom. Therefore, it was expected that under this labeling system, configuration "A" would have the highest NO_x emission rates, and "D" the lowest.

From the data collected on NO_x vs register settings, it soon became apparent that NO_x emissions were not significantly affected by register settings alone and no particular trends or patterns were exhibited. This is discussed in more detail in Section 4.1.

Effects on other emissions (tabulated in Appendix B) have also been analyzed in a similar fashion, and the same conclusion has been drawn; register settings in themselves show no discernable trends and have only an insignificant effect on emissions. Significant effects on emissions are achieved only when register setting adjustments are coupled with changes in other operating parameters.

3.1.2 Effect of Firing Mode on NO_x Emissions

This parameter is a measure of how the total fuel feed is distributed among the boiler's 24 burners. The boiler's control system allows fuel to be partially or fully shut off to any one or more of the 6 rows of burners (3 rows on each of two walls - Figure 2-2). When fuel to any row of burners is shut off, primary air flow stops but if the registers are not closed, secondary air flow continues to flow through the burner throats. When this was done on a top row, that row behaved like a source of "over-fire-air" (OFA). Normal practice requires the registers to close when a mill is brought off-line. But, during this program, since registers could not be closed when mills were brought off-line, the effect of biasing was reduced or minimized when a center or bottom level mill was out of service.

Eighteen firing modes (Table 3-6) were tested at Crist No. 7. Of course, not every firing mode could be tested at every load. For example, it would have been impossible to achieve full load using firing mode #14 in which one third of the burners are off.

Generally, NO_x emissions were lowest when fuel was distributed in a manner that made the bottom burners fuel-rich, and the top burners fuel-lean. (Staged combustion.) This concept was considered as identification numbers were assigned to the eighteen firing patterns tested. The highest ID numbers were assigned (Table 3-6) to those firing patterns where, at the top

TABLE 3-6

FIRING PATTERN NOMENCLATURE

(SEE FIGURE 2-2 FOR IDENTIFICATION NUMBERS AND LOCATIONS OF BURNER ROWS AND INDIVIDUAL BURNERS)

← Best for NO_x Control

Worst NO_x Emitters (Expected) →

ID	BURNER CONFIGURATION	
	General Description	Specific Description
1	Both Bottom Rows Off	B&E No Fuel (Air Only)
2	Two Bottom Rows on Same Side Off	D&E or A&B No Fuel (Air Only)
3	Extra Coal to Top Two Rows	C&F Fuel-Rich
4	One Bottom Row Off	E No Fuel (Air Only)
5	All Burners on Nearly Equally	A, B, C, D, E, & F on Equal
6	One Middle Row on Gas (Not Coal)	D on Gas (Not Coal), Rest on Coal
7	One Middle Row Off	D or A No Fuel (Air Only)
8	One Top Row and One Middle Row on Opposite Sides, Off	D&F No Fuel (Air Only)
9	Both Top Rows Fuel-Lean; One Bottom Row Off	C&F Lean, E No Fuel (Air Only)
10	One Top Row Fuel Lean	C or F Lean
11	Both Top Rows Fuel-Lean	C&F Lean
12	One Top Row Off, Next Row Down Firing Gas	C No Fuel (Air Only), D on Gas
13	One Top Row Off	C or F No Fuel (Air Only)
14	Two Top Rows on Same Side Off	C&D No Fuel (Air Only)
15	Both Top Rows (Opposite Sides) Off	C&F No Fuel (Air Only)
16	Both Top Rows and One Bottom Row Off	C, F, & B No Fuel (Air Only)
17	One Top Row and Both Middle Rows Off	F, A, & D No Fuel (Air Only)
18	Three Topmost Rows Off	C. D, & F No Fuel (Air Only)

Notes:

- All burners not mentioned may be assumed to be on and firing coal at equal rates.
- Secondary air dampers are set in fixed position, hence, air flow distribution is independent of fuel distribution. For example, when fuel is shut off to a burner row, air continues to flow through those burners.

burner elevation, the fuel/air ratio was lowest (relative to the f/a ratio for the lower burners). Hence, it was expected that the highest numbered firing patterns (highest degree of staging) would produce the least NO_x. As expected, Figure 3-1 shows that NO_x emissions were lowest, for the firing patterns with the highest ID numbers.

3.1.3 Effect of Load on NO_x Emissions

Load is the amount of electricity being produced by the boiler's driven generator. Of course, as load is decreased, the boiler requires less fuel, and less heat is radiated over the same collection area. The result is a cooler fire, and consequently less NO_x. However, for good operation, lower loads require higher excess air levels. These two parameters have competing effects on NO_x emissions. Hence, a minimum NO_x level with respect to load may exist.

The various loads tested were grouped into three categories:

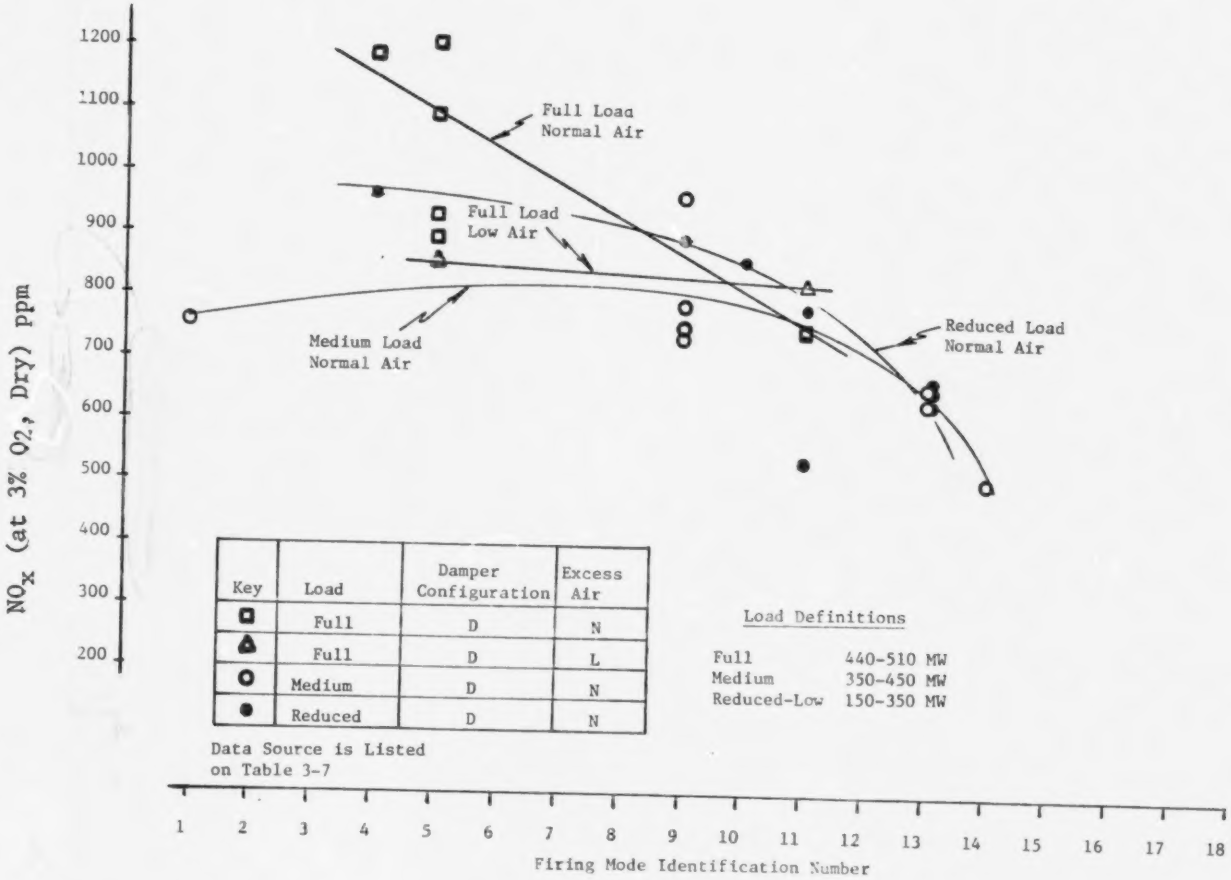
o Full or near full	(440-510 MW)
o Reduced	(350-450 MW)
o Low to medium	(150-350 MW)

For the purpose of analysis, these categories were allowed to overlap. Most tests were done at the higher loads since demand for electric power requires the boiler to operate at high load most of the time. Generally, load cannot be varied at will. It must follow demand. Hence, load is normally not considered as a useful method for the control of NO_x emissions. However, there may be instances such as severe adverse meteorological episodes where it may be desirable to limit NO_x emissions through a reduction in load. The effect of load reductions on NO_x emissions, therefore, is of interest.

Figure 3-2 is a plot of NO_x emissions vs load for the tests listed in Table 3-8. It may be observed that NO_x decreases with load and the rate of decrease is more pronounced (steeper slope) at the higher loads. The magnitude of NO_x reductions with load will vary in each boiler and should be determined individually to determine the range of reductions possible.

3.1.4 Effect of Excess Air on NO_x Emissions

Air is necessary to oxidize the fuel as it burns. But air reacts to form thermal and fuel NO_x. Furthermore, some of the energy used to heat the excess air is then lost with the hot gases leaving the stack. The result is decreased efficiency. So, it might seem wise to minimize excess air. But too little air will result in incomplete combustion. Clearly an optimum



Key	Load	Damper Configuration	Excess Air
▢	Full	D	N
△	Full	D	L
○	Medium	D	N
●	Reduced	D	N

Data Source is Listed
on Table 3-7

Load Definitions

Full	440-510 MW
Medium	350-450 MW
Reduced-Low	150-350 MW

Figure 3-1. NO$_x$ vs. Firing Mode.
(For Damper Configuration "D")

TABLE 3-7

KEY TO FIGURE 3-1*
(NO_x VS. FIRING MODE)

Load	Damper Configuration		Air Flow	DATA SOURCE Test Numbers for Indicated Firing Modes																	
	ID	(T-M-B)		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Full Load (440-510 MW)	A	(33-33-33)	Normal					1,1A,122 122A	31	59,60 61											
	B	(40-30-40)	Normal			128		3,1B,1C,3A,1E, 202,201,205, 206,100B,123, 125,126,129						7							
	B	(40-30-30)	Low					4,4A,204A,204B						8,4C,4D, 4E,137							
	D	(60-25-15)	Normal*				73	71,72,81,82						83, 84B							
			Low*					80						85							
Reduced Load (350-450 MW)	A	(33-33-33)	Normal							56,57						63					
			Low								58					64					
	B	(40-30-30)	Normal				203, 204	1D, 150, 152, 200		127,131 132				7A	32	11,11A, 11B,11C					
			Low											8A		12,12A					
	C	(55-25-20)	Normal					104						91,93		106					
			Low					105						92,94, 102		89,90,107					
	D	(60-25-15)	Normal*				78					74	69	98,103		65,66,67					
Low-Med. (150-350)	A	(33-33-33)	Normal		55						53					62				50,51,52	54
	B	(40-30-30	Normal	23	130			135			33					133		17,17A	34		
			Low	24												134,136		18,18A			
	D	(50-30-30)	Normal*	88								75, 76, 77, 79				86,87	68				

*The four curves in Figure 3-1 represents the four rows marked by asterisks above, respectively.

Note: The table also contains references to other data not used in Figure 3.1.

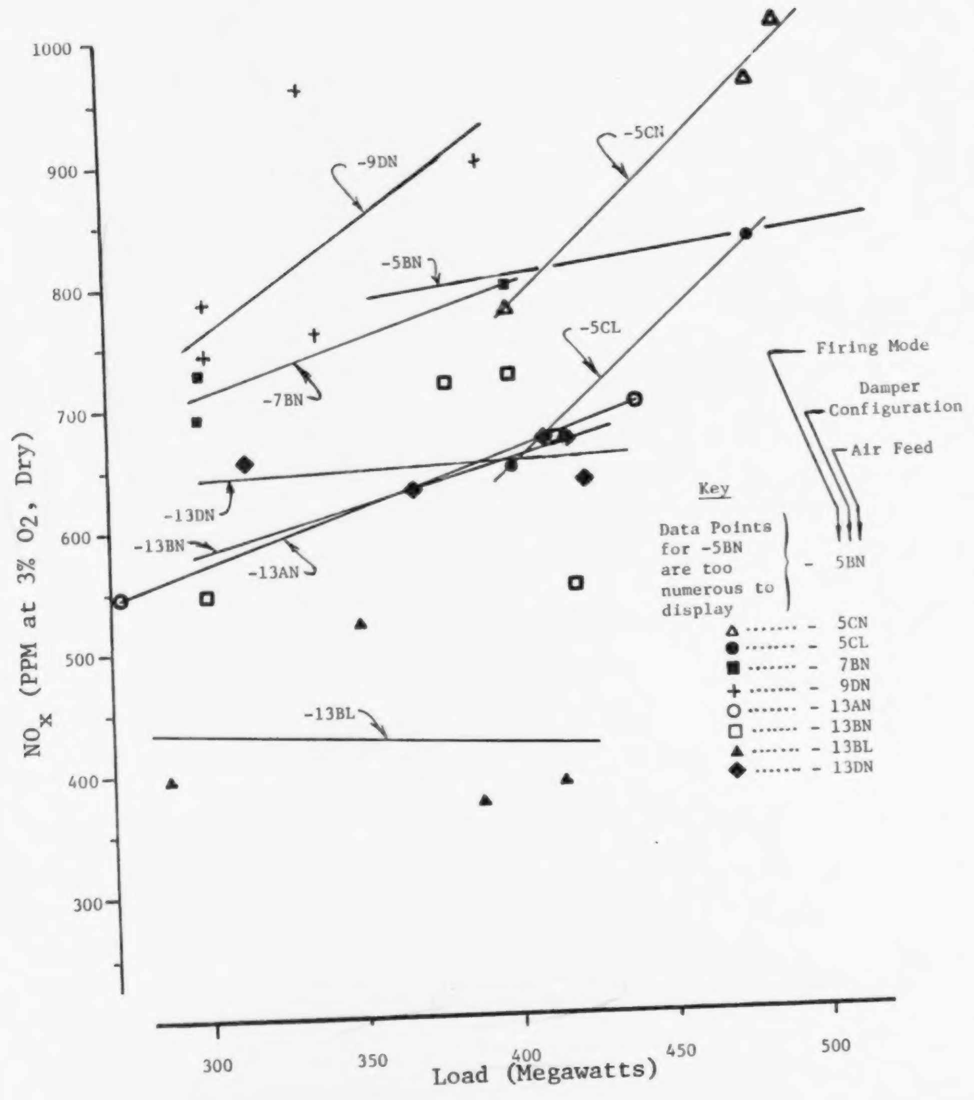


Figure 3-2. NO_x vs. load (see Table 3-8 for data source).

TABLE 3-8

KEY TO FIGURE 3-2 : NO_x VS. LOAD

Code**	Firing Mode	Damper Configuration	Air Flow	Data Source (Test Numbers)
* See Note	5	A (33-33-33)	Normal	1, 1A, 122, 122A
-5BN		B (40-30-30)	Normal	1B, 1C, 1D, 1E, 3, 3A, 100B, 123, 125, 126, 129, 135, 150, 152, 200, 201, 202, 205, 206
* See Note			Low	4, 4A, 204A, 204B
-5CN		C (55-25-20)	Normal	100, 104, 124
-5CL			Low	101, 105
* See Note	7	A (33-33-33)	Normal	56, 57, 59, 60, 61
-7BN		B (40-30-30)	Normal	127, 131, 132
-9DN	9	D (50-25-15)	Normal	74, 75, 76, 77, 79
* See Note	11	B (40-30-30)	Normal	7, 7A
* See Note			Low	4C, 4D, 4E, 8, 8A, 137
* See Note		C (55-25-20)	Low	92, 94, 102
* See Note		D (50-25-15)	Normal	83, 84B, 98, 103
* See Note			Low	85, 95
-13AN	13	A (33-33-33)	Normal	62, 63
-13BN		B (40-30-30)	Normal	11, 11A, 11B, 11C, 133
-13BL			Low	12, 12A, 134, 136
* See Note		C (55-25-20)	Low	89, 90, 107
-13DN		D (50-25-15)	Normal	65, 66, 67, 86, 87

Note:

*Data sets indentified with an asterisk were not plotted due to a sparsity of data points or, small range of loads covered.
**Code = last 3 elements of operating condition abbreviation: firing mode, register configuration, excess air flow.

exists. The boiler manufacturer has established guidelines which the boiler operators use to control the amount of air entering the boiler. This amount varies according to load. For example; at lower loads, the total air flow is decreased, but since fuel flow is decreased even more, the ratio of air to fuel is actually increased at lower loads. Generally, excess air can be maintained constant over a considerable load range as long as the unit remains within its steam temperature control range. However, as load is further reduced, excess air must be increased in order to maintain adequate bulk gas mixing in the furnace and prevent steam temperature from falling too quickly. Under minimum load conditions (one or two mills in service) there must be a minimum of air flow to ensure adequate unit purging. Operators can achieve optimum excess air by using both CO and O_2 monitors. However, in order to optimize unit performance the correct relationship between combustion efficiency, air flow and steam conditions must be maintained.

Manufacturer-supplied guidelines for boiler operators generally specify a wide range of allowable excess air levels for boiler operation. This gives boiler operators considerable flexibility in the control of the boiler. The optimum amount of excess air for NO_x control usually lies within the range specified by the manufacturer and may be at the manufacturer's "design" level of excess air. Through this program, the range in which the optimum lies, was found or confirmed for each load range tested.

The terms "excess air," "total air flow," and "amount of O_2 in the flue gas" are used almost interchangeably. All refer to the overall fuel/air stoichiometry of the combustion process. Perhaps the most quantitative descriptor is the "amount of O_2 in the flue gas." It is easily measured in the flue gas samples.

Figure 3-3 presents a plot of NO_x vs percent O_2 in the flue gas (a measure of excess air) for the full load data tabulated in Table 3-9 in which firing mode 5 was used. It may be seen that NO_x emissions decrease with decreasing O_2 levels in the flue gas and that for the range tested the rate of decrease is influenced by the secondary air register configuration employed.

Figure 3-4 is illustrative of the effect of O_2 on NO_x emissions and the O_2/CO relationship for tests conducted on the Crist No. 7 boiler at full load operation. The decrease in NO_x emissions with decreasing O_2 may again be noted. The corresponding relationship between O_2 and CO emissions, however, may be noted to be a relatively gradual increase of CO as O_2 is decreased until a point is reached where CO increases rapidly. Normally this breakpoint is in the neighborhood of 200 ppm CO, the arbitrary limit established in this investigative program beyond

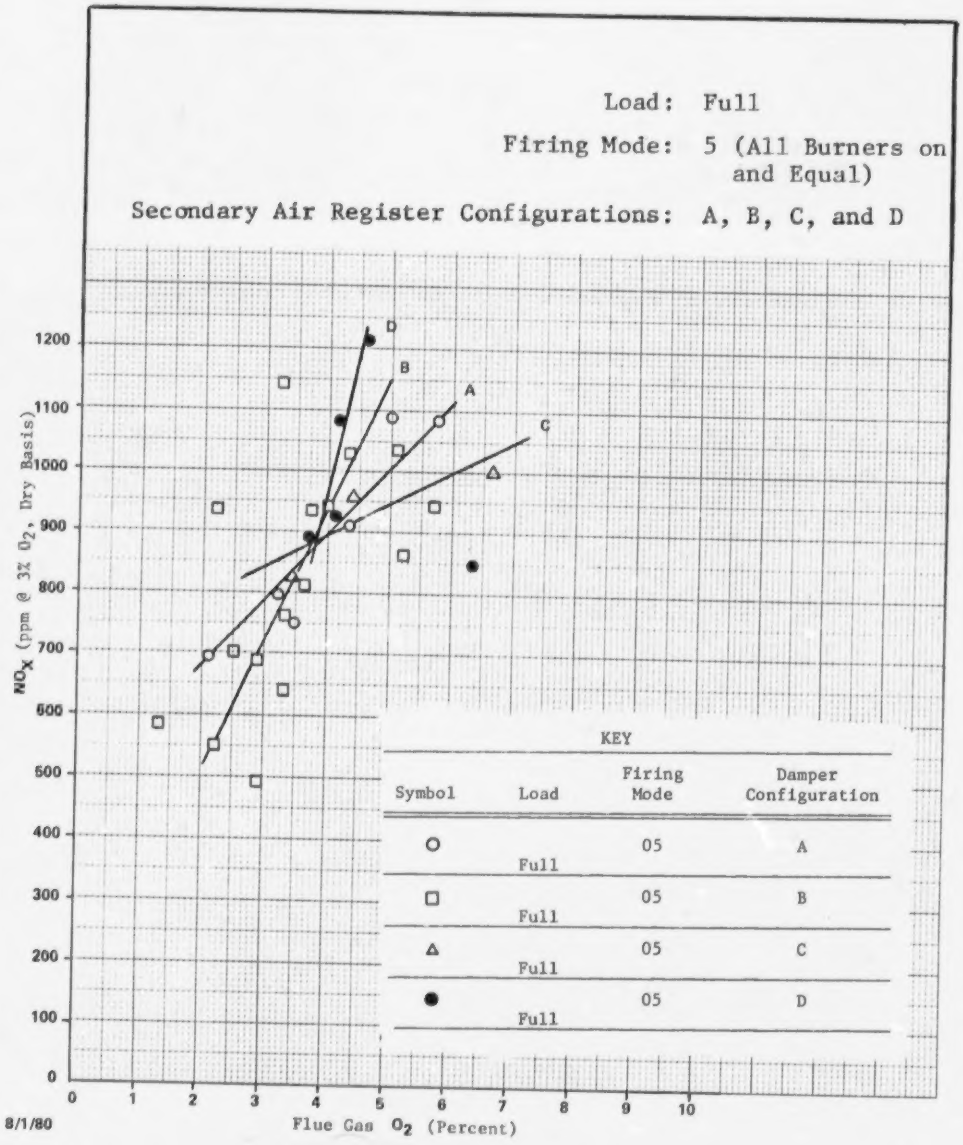


Figure 3-3. NO_x vs. O_2 for Various Air Register Settings (See Table 3-9 for Data Source).

TABLE 3-9

KEY TO FIGURES 3-3 AND 3-4
NO_x AND/OR CO VS. EXCESS AIR

Load	Firing Mode	Register Configuration		Data Source for Figure
(MW)		ID	(T-M-B)	(Test Numbers)
Near Full (440-510)	5	A	(33-33-33)	1, 1A, 2, 2A, 122A
		B	(40-30-30)	1B, 1C, 1E, 3, 4, 4A, 100B, 123, 125, 126, 129, 201, 202, 204A, 204B, 205, 206
		C	(55-25-20)	100, 101, 124
		D	(60-25-15)	71, 72, 80, 81, 82
	11	B	(40-30-20)	4C, 4D, 4E, 7, 8, 137
		D	(60-25-15)	83, 84B, 85
Reduced (350-450)	5	C	(55-25-20)	104, 105
	11	B	(40-30-30)	7A, 8A
		C	(55-25-20)	91, 92, 93, 94, 102
		D	(60-25-15)	95, 98, 103
	13	A	(33-33-33)	63, 64
		B	(40-30-20)	11, 11A, 11B, 11C, 12, 12A
		C	(55-25-20)	89, 90, 106, 107
Low-Medium (150-350)	1	B	(40-30-20)	23, 24
	13			133, 134, 136
	15			17, 17A, 18, 18A
		C	(55-25-20)	117, 118

See Figure 3-3

See Figure 3-4

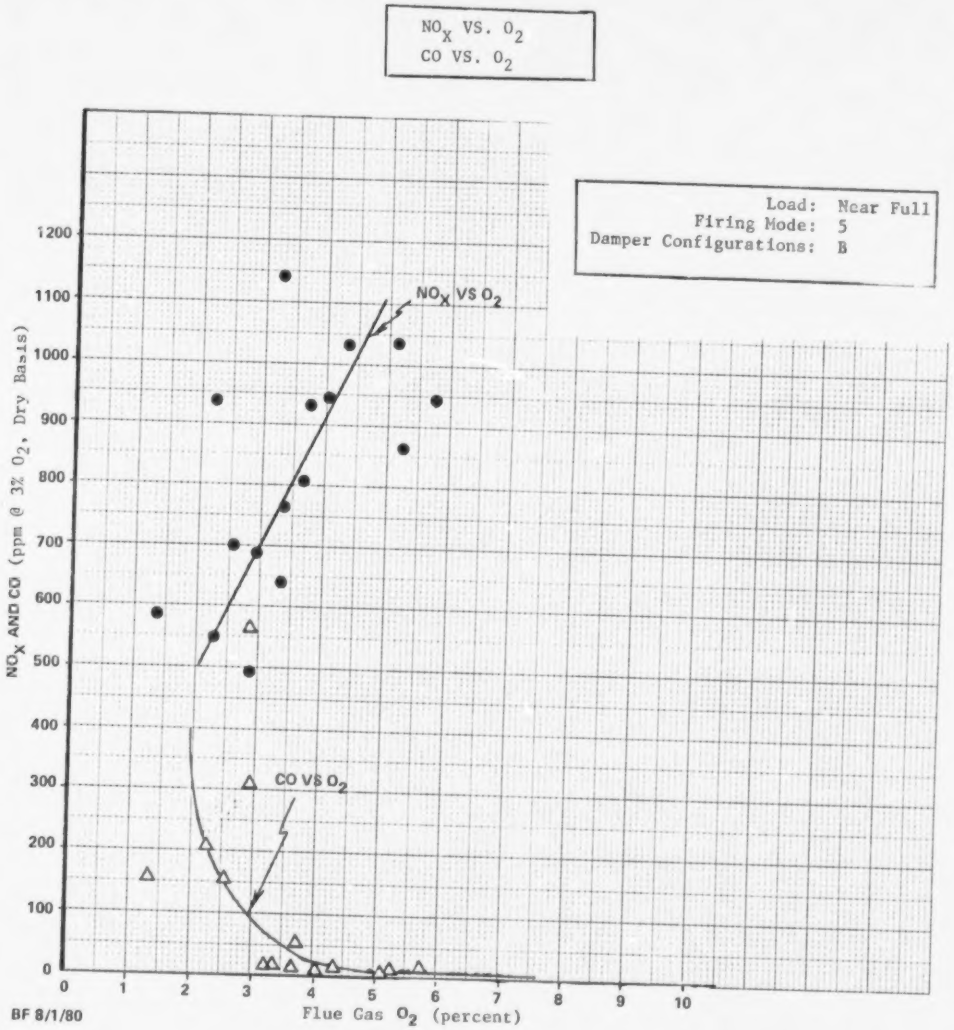


Figure 3-4. NO_x and CO vs. O_2
(See Table 3-9 for Data Source).

which the air supply should not be decreased. This breakpoint is also dependant on the design of the boiler and combustion system, the limits of which must be established for each mode of operation to properly optimize emissions.

3.1.5 Effect of Partial Staging on NO_x Emissions

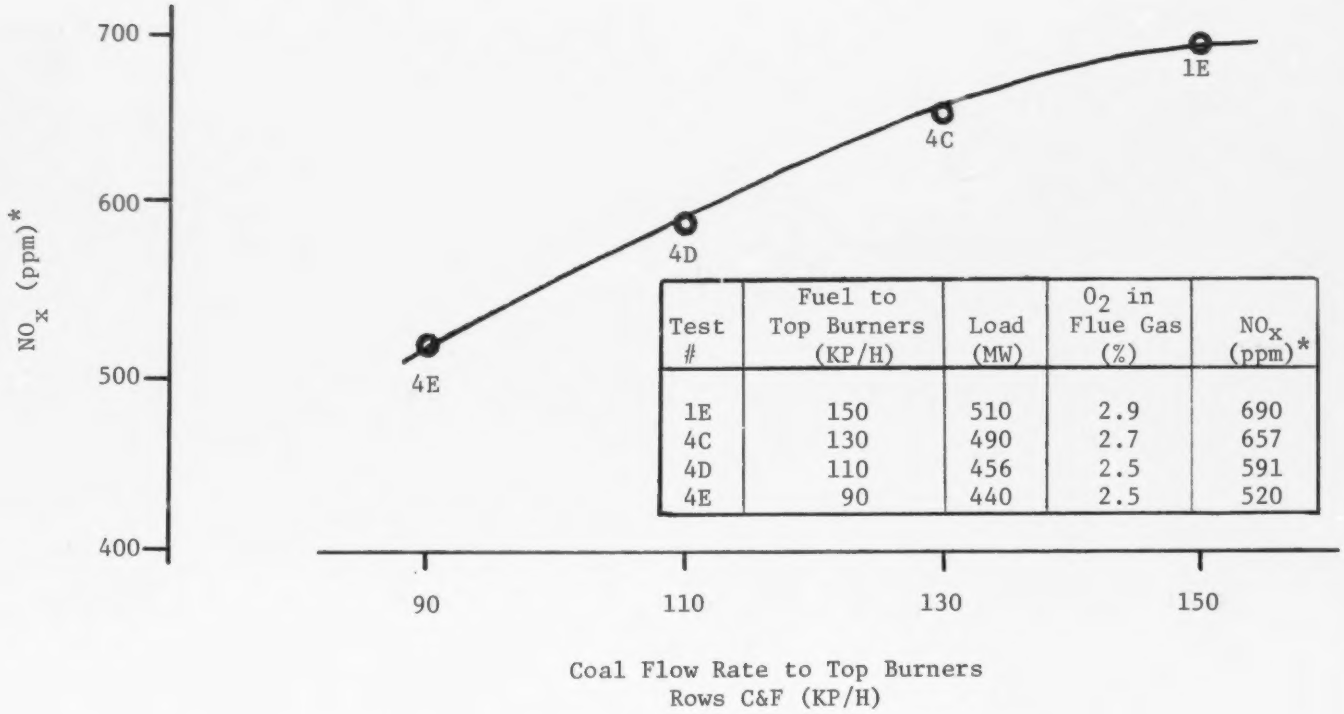
Staging is a combination of firing mode and register setting adjustments which cause the bottom burners to operate fuel-rich, and the top to be fuel-lean. When used in combination with low excess air firing, staging of the combustion process has been found to be an effective combustion modification for NO_x control. However, full load operation of the Crist No. 7 boiler could not be maintained under normal staging practices, when top burners were taken out of service for use as overfire air ports. Instead, a pseudo-staging process had to be employed by biasing the fuel flow between the top and bottom burners, operating the top burners fuel-lean and those on the bottom fuel-rich, while maintaining low excess air operating levels. This was accomplished by decreasing the fuel flow to the top burners while maximizing the flow to the bottom burner rows to achieve a staging effect. Substantial NO_x reductions were achieved in this manner but not nearly as effectively as with full staging, and at the expense of some load carrying ability (13% reduction).

Figure 3-5 is illustrative of the low excess air, staged firing, low-NO_x operation maintained on the Crist No. 7 boiler at or near full load output (500 MW). It may be seen from Figure 3-5 that full load could be carried on the boiler while firing 150,000 pounds of coal per hour in the top burners with 2.9% O_2 in the flue gas (usually 4 to 4.5% O_2 for normal operation). Under these conditions of decreased excess air, NO_x emissions were 690 ppm, well below normal baseline emissions of 900 ppm. This decrease is partially due to the low excess air as seen from the relationship between NO_x and O_2 presented in Figure 3-4. As coal flow was decreased progressively in the top burners, corresponding decreases occurred in load and NO_x emissions. However, the indicated reduction (23%) is not entirely due to staging. Decreased load (70 MW or 13%) is partially responsible for the decrease in NO_x emissions as shown in Figure 3-2. Furthermore, the 1.4% decrease in O_2 between test data points 1E and 4E is responsible for some of the NO_x decrease as supported by Figure 3-4.

3.1.6 Optimum CM for NO_x Control

Typically, before this test program, normal boiler operating parameters for full load were as follows:

- All secondary air registers set at 50% open (configuration "A").



Test #	Fuel to Top Burners (KP/H)	Load (MW)	O_2 in Flue Gas (%)	NO_x (ppm)*
1E	150	510	2.9	690
4C	130	490	2.7	657
4D	110	456	2.5	591
4E	90	440	2.5	520

*Dry basis, corrected to 3% O_2.

Figure 3-5. Staged combustion: NO_x vs. degree of staging.

- All burners on and firing equally (firing mode "05").
- Normal total air flow.

NO_x emissions for these "as found" (uncontrolled) or "baseline" tests (1, 1A, 122 and 122A (Table 3-5)) averaged 960 ppm (at 3% O_2, dry basis).

The highest NO_x emissions (chemiluminescent measurement method - Appendix B) observed at Crist No. 7 were seen during Tests 71, 73, and 202; averaging 1190 ppm (at 3% O_2, dry). However, for Test No. 202 the total air feed rate was unusually high. The reader should also note that for Test No. 73, one bottom row of burners was off (air only); a routine operating procedure for this boiler...especially when not at full load. During Test No. 71, all burners were firing coal equally.

Perhaps the most conservative way of expressing the baseline, full load NO_x emission rate, would be to define it as the average of all the NO_x emission rates measured when the boiler was operated at 440 MW or more, with normal air flow and all burners on equally (test numbers 1, 1A, 1B, 1C, 1E, 3, 3A, 71, 72, 81, 82, 100, 100B, 122, 122A, 123, 124, 125, 126, 129, 201, 202, 205, and 206). This group does not include "high-NO_x" firing mode tests, such as No. 73, even though such firing modes were not unusual in "as-found" operating procedures. The group of tests does, however, include many tests run with "low-NO_x" damper configurations, and many that were run at somewhat less than full load (<500 MW). In other words, the tests in this "baseline" group include many test that were run at conditions known to give lower NO_x emissions than "worst case" conditions. Hence, this conservatively defined group of "baseline" tests will yield an under-inflated value of "baseline NO_x emission rate."

In accord with assumptions listed in the preceding paragraph, the average full-load NO_x emission rate for the "baseline" group has been calculated to be 913 ppm (at 3% O_2, dry basis).

Similarly, the boiler's full load NO_x emissions when operated in the "low-NO_x" mode, have been calculated to be 723 ppm (at 3% O_2, dry basis). This is based on the average NO_x emissions from all tests where the boiler was operated at 440 MW or more with firing mode No. 5 or higher and low total air flow (test numbers 2, 2A, 4, 4A, 4C, 4D, 4E, 8, 80, 85, 101, 137, 204A, and 204B).

Hence, one can conclude that at full load, the NO_x emission rate can be decreased by approximately 22% through use of combustion modifications.

The largest NO_x decreases were obtained by decreasing O_2 from the typical operating level to the manufacturer's design level. The effects of biased firing were not as great as those of decreased excess air.

Since the boiler does not spend as much time at the lower loads, the analysis was not carried out at lower loads. Furthermore, at reduced loads, the furnace is cooler and NO_x concentrations (ppm) in the flue gas are decreased; and, since total flue gas flow rate is also decreased at lower loads, the NO_x mass flow rate (pounds/hour) is doubly decreased. Clearly the major concern is NO_x emissions in the upper load range, and it has just been shown that such emissions can be decreased by about 20% through use of combustion modifications for NO_x control.

After many boiler characterization tests, a set of guidelines (Table 3-9.1) was developed which suggested to Crist No. 7 operators, alternative ways of running the boiler so that NO_x emission rates might be decreased.

The "low-NO_x" period of operation officially began in October of 1976, and ended with panel removal, approximately April, 1978. The boiler actually ran a total of about 12 months during this ~17 month period. (During this time the unit was out of service for conversion from pressurized to balanced draft operation.) Control room records indicate that during that time, a moderately reasonable attempt was made to follow the "low-NO_x" guidelines, but perhaps other problems prevented those guidelines from being used as often as originally expected.

Table 3.9-1 is a summary of those guidelines:

TABLE 3-9.1
LOW-NO_x GUIDELINES

WHEN AT THIS LOAD	USE THESE COMBUSTION PARAMETERS	
	Coal Feeds	Flue Gas O_2
Full (450-520)	Top two mills (C&F) cut back as far as possible	2.5 - 3.0% (a)
440-450 MW	Shut off one top mill (C or F), then cut back as far as possible on the other top mill	3.5 (b)
175-320 MW	Shut off both top mills (C&F)	5.0 (c)

(a) Was typically 4.5 before "low-N
(b) Was typically 6.0 before "low-NO_x" guidelines.
(c) Was typically 8.0 before "low-NO_x" guidelines.

During the "low-NO_x" operating period, the secondary air registers were set so that most of the air entered the boiler through the top burner rows (C&F) with less going to the bottom two elevations of burners. (Rows C&F were ~60-70% open while A, B, D, and E were ~30-40% open.)

Essentially, the guidelines suggest that low total air flow should be used in combination with staged combustion and over-fire-air with upper burners as fuel lean as possible.

During the "low-NO_x testing," the only other emission significantly affected by combustion modifications for NO_x control was CO. Generally, when NO_x was reduced by more than 20%, CO emissions might increase to 150 ppm (from 30 ppm). Any problem with CO emissions could be eliminated by use of a CO monitor during set-up of the boiler. If the boiler had been equipped with a permanent continuous CO monitor, the operators could decrease NO_x emission levels by decreasing and maintaining boiler excess air closer to design.*

Low-NO_x operation caused only slightly higher CO concentrations in the upper regions of the furnace zone (see Section 3.3.1).

3.2 Furnace Waterwall Fireside Corrosion Results

3.2.1 Corrosion Probes

Section 2.3.1 provided background on the use of corrosion probes to develop corrosion rate data which would be indicative of the rate of corrosion experienced on actual furnace tubes. It was pointed out that the corrosion probe investigative program conducted on Gulf Power Company's No. 7 boiler at the Crist Station was amplified extensively over previous work in order to obtain data on the effect of corrosion with time for potential correlation with actual furnace tube corrosion. Instead of exposing probes for 300 hours only, exposure at 30 hours to show the effects of initial corrosion and 1000 hours to show the effect of longer term corrosion, were added. These modifications to the corrosion probe program result in different implications regarding corrosion rates.

Corrosion rate data developed on the No. 7 boiler at the Crist Station under varying exposure times are given in Tables 3-10 through 3-17. As expected, initial corrosion rate data, obtained in 24 to 30 hour exposure tests are considerably higher than for 300 hour or longer exposure periods. Tables 3-10, 3-11, and 3-12 show that in these short term tests, average corrosion rates (for each probe) varied from 62.9 to 113.6 mils per year. Under low NO_x conditions (Table 3-10) probes exposed in the

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*Typical O_2 at full load is 4.5%. FW's design O_2 at full load is 3.3%, but is not safely achievable without a CO monitor.

TABLE 3-10

24 HOUR, LOW NO_x CORROSION RATE DATA (BY PROBES)

Probe No.	Location	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
1	Right Wall (129.8')	Low NO_x	24	136.2 91.0(*)	113.6
2	Right Wall (157.8')	Low NO_x	24	68.1 110.4(*)	89.3
4	Left Wall (157.8')	Low NO_x	24	87.5 97.1(*)	92.3

Note:

(*) Coupon closest to furnace wall

TABLE 3-11

25 HOUR BASELINE CORROSION RATE DATA (BY PROBES)

Probe No.	Location	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
1	Right Wall (129.8')	Baseline	25	80.2(*) 53.6 82.7	72.1
2	Right Wall (157.8')	Baseline	25	75.2(*) 56.4 57.0	62.9
4	Left Wall (157.8')	Baseline	25	116.4(*) 85.0 73.3	91.6

Note:

(*) Coupon closest to furnace wall

TABLE 3-12

30 HOUR BASELINE CORROSION RATE DATA (BY PROBES)

Probe No.	Location	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
2	Right Wall (157.8')	Baseline	29.8	108.9(*) 116.9 51.3	92.4
4	Left Wall (129.8')	Baseline	30.0	100.5(*) 59.9 161.6	107.3

Note:

(*) Coupon closest to furnace wall

TABLE 3-13

180 TO 260 HOUR LOW NO_x CORROSION RATE DATA (BY PROBES)

Probe No.	Location	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
1	Right Wall (129.8')	Low NO_x	256.0	31.9(*) 33.5 31.0	32.1
2	Right Wall (157.8')	Low NO_x	261.1	25.8(*) 22.0 17.0	21.6
3	Right Wall (129.8')	Low NO_x	182.0	14.3(*) 15.2 20.6	16.7
4	Left Wall (157.8')	Low NO_x	261.2	17.8(*) 7.6 7.9	11.1
Avg.					20.4 Avg.

Note:

(*) Coupon closest to furnace wall

TABLE 3-14

290 HOUR BASELINE CORROSION RATE DATA (BY PROBES)

Probe No.	Location	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
1	Right Wall (129.8')	Baseline	294.3	47.4 9.1 12.6(*)	23.0
2	Right Wall (157.8')	Baseline	291.8	9.7 5.3 11.7(*)	8.9
3	Left Wall (129.8')	Baseline	293.2	46.3 27.9 19.3(*)	31.2
4	Left Wall (157.8')	Baseline	289.3	88.0 21.5 19.5(*)	43.0
Avg.					26.5 Avg.

Note:

(*) Coupons closest to furnace wall

TABLE 3-15

290 HOUR BASELINE AND LOW NO_x CORROSION RATE DATA (BY PROBES)

Probe No.	Location(**)	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
1	Left Wall	Baseline	286	25.7(*) 20.8 32.6	26.4
2	Left Wall	Low NO_x	288	11.6(*) 10.2 16.8	12.9

Notes:

(*) Coupon closest to furnace wall

(**) Probes located in side walls 2 1/2 feet (0.8 m) above top burner centerline

TABLE 3-16

597 AND 738 HOUR LOW NO_x CORROSION RATE DATA (BY PROBES)

Probe No.	Location	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
4	Left Wall (157.8')	Low NO_x	597	9.3(*) 11.7 18.9	13.3
2	Right Wall (157.8')	Low NO_x	738	8.3(*) 9.3 11.0	9.5

Note:

(*) Coupon closest to furnace wall

TABLE 3-17

1000 HOUR BASELINE CORROSION RATE DATA (BY PROBES)

Probe No.	Location	Firing Condition	Exposure Time, Hrs.	Coupon Corrosion Rate Mils/Year	Average
2	Right Wall (157.8')	Baseline	996.5	10.2(*) 7.9 5.9	8.0
3	Left Wall (129.8')	Baseline	999.0	15.8 11.4 9.1(*)	12.1
4	Left Wall (157.8')	Baseline	997.2	15.9(*) 15.1 15.9	15.6

Note:

(*) Coupon closest to furnace wall

expected high corrosion area of the furnace at the burner levels (129.8 ft) for 24 to 30 hours experienced greater corrosion than probes located outside of the burner burner areas (157.8 ft), i.e., 113.6 vs 90.8 mils/year, average, respectively. A similar trend is evident under baseline conditions, especially as exhibited in Table 3-12, but the differences are far less pronounced.

Corrosion rate data developed in probe exposures ranging from 182 to 294.3 hours are listed in Tables 3-14 through 3-15. As in previous tests, corrosion rates are relatively low (overall average of about 22.7 mils/year) and quite consistent. Referring to Table 3-14 for baseline operation, it may be seen that the average corrosion rate was 26.5 mils/year. For low-NO_x firing, in tests lasting about 200-300 hours, (Table 3-13) corrosion as measured by probes averaged 20.4 mils/year or about 6 mils/yr lower than for comparable baseline tests on Table 3-14. These differences are not viewed as being of particular significance. For baseline operation, Table 3-14 shows that probes in the more vulnerable burner area (129.8') averaged 27.1 mils/year vs 25.9 mils/year for those at the upper level of 157.8 ft. Under low-NO_x conditions (Table 3-13), however, difference ratios are somewhat greater, i.e., 24.4 vs 16.4 mils/year for probes at the 129.8' and 157.8' levels, respectively. While the magnitude of the latter differences are significant, it is doubtful that much importance should be attached to them since data developed in longer term tests (discussed below) show no appreciable differences).

Data tabulated in Table 3-15 were obtained with probes inserted in slag blower openings in the boiler sidewalls at a location 2 1/2 ft above the top burner centerline. Conditions at this location would be expected to approximate those at 129.8 ft elevation and results obtained are, in fact, comparable.

Tables 3-16 and 3-17 present corrosion rate data developed in longer-term tests ranging from 597 to 999 hours. Referring to the tables it may be noted that average corrosion rates are significantly lower and more consistent than for probes exposed at 30 to 300 hours. Location of the probes within the boiler does not appear to be a factor. Also, average corrosion rates for probes exposed to baseline firing conditions for approximately 1000 hours, ranging between 8.0 and 15.6 mils/year, are comparable to rates of 13.3 and 9.5 mils/year average developed on probes exposed to low-NO_x operating conditions for 597 and 738 hours exposure, respectively.

A comparison of corrosion rate data developed on Gulf Power Company's No. 7 boiler at the Crist Station is better illustrated in Figure 3-6 showing a plot of corrosion rate vs exposure time for probes exposed to both baseline and low-NO_x firing conditions. Referring to Figure 3-6, it may be noted that coupon

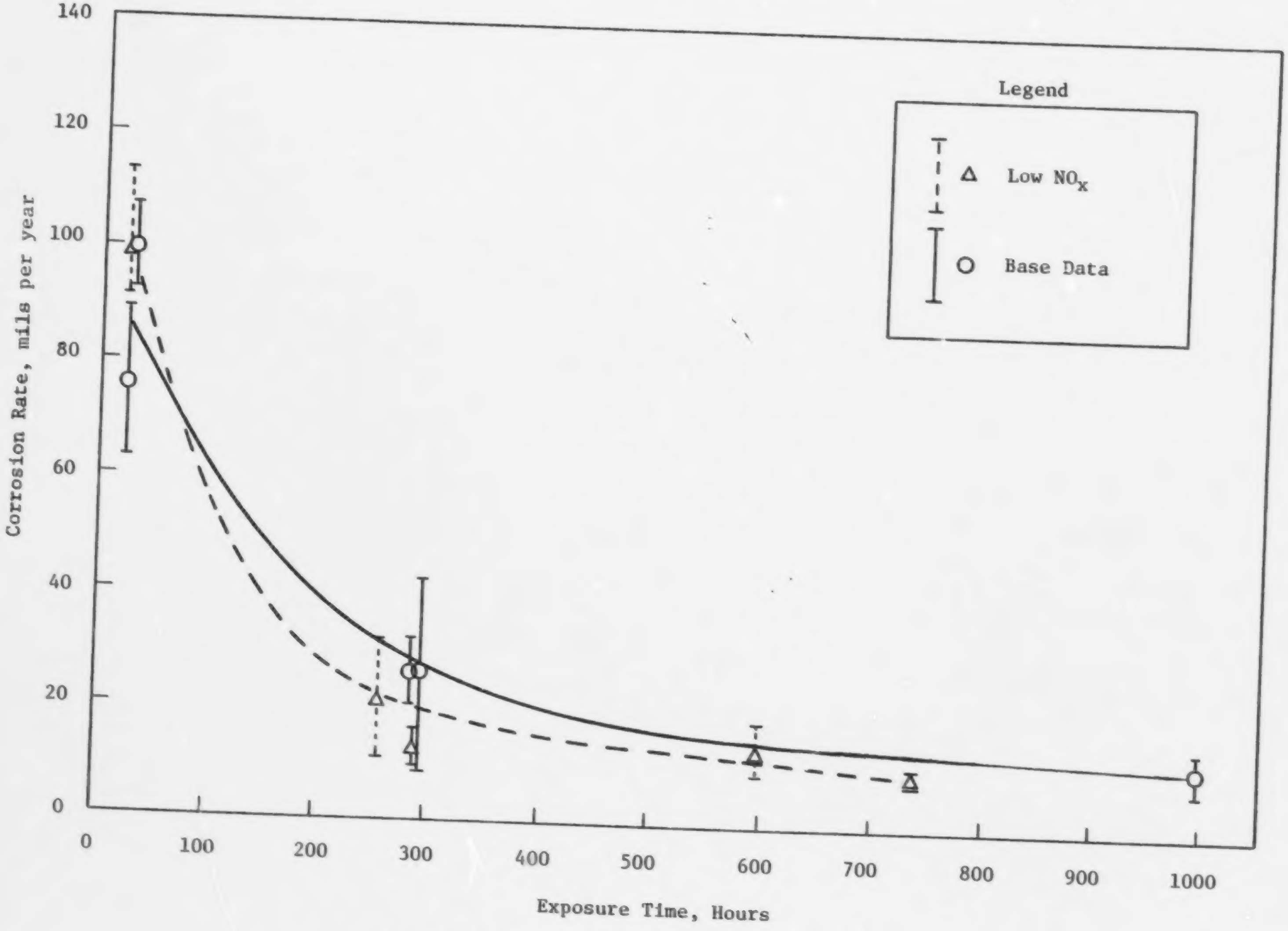


Figure 3-6. Comparison of Corrosion Rates Using Probes
Gulf Power Company, Crist Station, Boiler No. 7
Pulverized Coal Firing.

corrosion rates decrease with exposure time asymtotically up to 1000-hour exposure. Initital corrosion rates developed at 24 to 30-hours exposure are high with considerable scatter in the data. At 250 to 300 hours exposure, corrosion rates are much lower and more consistent in range. Above 450 to 500 hours exposure, corrosion rates level out to an average rate of 10 to 12 mils/year with very little scatter in the range of the data. These rates, however, are still much higher than the 1 to 3 mil/year wastage expected in actual furnace wall tubes. It is apparent from Figure 3-6 that corrosion probes should be exposed for a minimum of 450 hours if effective correlation is to be made with actual furnace tube corrosion.

It is concluded from these corrosion probe investigations that:

- o Corrosion rates developed via corrosion probes decrease with exposure time through 1000 hours approaching an asymtote above 450 hours exposure.

- o Corrosion probes exposed for short terms (up to 30 hours) within the burner areas in the furnace sidewalls experience greater corrosion rates than probes exposed outside the burner levels under low-NO_x firing conditions. A similar trend is indicated for baseline operating conditions but more data is needed to reach firm conclusions.

- o Probes exposed for periods of 300 to 1000 hours experienced no significant differences in corrosion rates due to furnace location (burner vs nonburner area) or furnace operating mode (baseline vs low-NO_x firing).

- o Effective correlation of actual long-term furnace tube corrosion rates require corrosion probe exposure of a minimum of 450 hour exposure.

3.2.2 Ultrasonic Measurements of Furnace Tubes

The plans and procedures used to obtain ultrasonic measurements of furnace tubes were described in Section 2.3.2. In this section, the measurement data will be presented and its statistical analysis discussed. The measurement program was designed to answer the following questions:

(1) What is the level of uncertainty or error in field ultrasonic measurements of furnace wall tube thickness?

(2) Does the furnace tube cleaning process result in biased corrosion rate measurement?

(3) Are corrosion rates of fireside furnace tube walls different at different furnace locations when exposed to (a) baseline operation and (b) staged combustion for "low-NO_x" operation?

(4) Are corrosion rates higher under "low-NO_x" operation than under baseline operation? Does this difference, if any, depend upon furnace location, i.e., side vs burner walls, within or outside burner elevation, etc.?

Because a special air injection system was installed in the hopper to clear up a slag problem, the test program might also provide some information on the possible effect of this hopper air injection system on corrosion rates in its vicinity.

During the initial measurement period (May, 1976), a special quality control procedure was used to determine ultrasonic measurement errors. A total of 61 individual tube points were measured twice on a "blind," predetermined random basis, once by Operator A and once by Operator B. Table 3-18 presents frequency tallies (for each wall-level measured) of the differences between the two independent measurements made on the same points. Statistics for each wall-level measured shown at the bottom of the table are: $\overline{\Delta}$, average difference; S_{Δ} , standard deviation of differences and n, the number of differences. The average and standard deviation of all 61 differences are -0.14 and 2.40 respectively. There is no evidence of high or low bias by either of the operators who made the measurements.

The variability in the measured differences can be converted into the estimated standard deviation of single measurements by dividing the standard deviation of difference of two measurements, 2.40 by $\sqrt{2}$ which gives 1.70. (It is assumed that the two measurements on each spot are independent and that the variability of each operator instrument combination is about equal.) Thus, the uncertainty or error of a single measurement in the field is about 1.7 mils and the error associated with the difference between two measurements is about 2.4 mils. Thus, if there were no other sources of variability (such as tube to tube variation, calibration error, variations from level to level within the furnace, etc.) the standard error of a single difference would be 2.4 mils, the standard error of an average of 4 paired differences would be $2.4/\sqrt{4}$ or 1.2 mils and the standard error of an average of 16 paired differences would be $2.4/\sqrt{16} = 0.6$ mils. However, as engineering experience on other boilers as well as on Crist No. 7 boiler indicates, other sources of variation do exist and these must be taken into account when analyzing corrosion data.

As described in Section 2, considerable effort was made in planning and executing the Crist No. 7 test program to obtain accurate estimates of changes, if any, in normal corrosion rates due to the cleaning process necessary to obtain ultrasonic tube wall thickness measurements. It was desired to provide assurance

TABLE 3-18

FREQUENCY TALLIES OF MEASUREMENT ERRORS -Δ

(Operator B Measurement Minus Operator A Measurement = Δ)

Δ = Operator B - Operator A (Mils)	Left Sidewall					Right Sidewall						Total
	Level Measured					Level Measured						
	1	2	3	4	5	1	2	3	4	5	6	
>7												
7						X						1
6												
5												1
4												
3		X		X								2
2	XX							X				3
1	XX	X			X			X				5
0	XXXX X	XX		XX		XXX	XXXX			X	XX	19
-1	XXXX		XXXX		X	XX	XX		X	XX		16
-2	X	X	X	X					X			5
-3												
-4	XXX											3
-5	X											1
-6	XX											2
-7						X						1
-8						X						1
<8	Ⓧ	Ⓧ										③
$\overline{\Delta}$	-0.72	-0.65	-0.80	0.75	0.40	0.00	-0.66	2.00	-0.75	-0.03	+0.15	-0.14
S_Δ	2.67	3.99	0.63	2.21	1.13	4.01	1.40	0.85	0.49	0.47	0.21	2.404
n	22	5	5	4	2	7	7	2	2	3	2	61

Note:

$\overline{\Delta}$ = Average difference, mils
S_Δ = Standard deviation of differences, mils
n = Number of differences
○ = Suspected outlier data (circled)

that the furnace tube cleaning and measurement process does not produce biased corrosion estimates or conclusions even though the process does result in changing the corrosion rate up or down in either (or both) normal and staged combustion operation. To review how this objective was accomplished, consider the first two measurements on tube numbers 1 and 5 of the left side wall at level 1 as shown below in Table 3-19.

TABLE 3-19

TUBEWALL THICKNESS MEASUREMENTS-MILS

Tube No.	(1) 5/76	(2) 10/76	(2)-(1)	Result
1	319.5	317.2	-2.3	Possible Bias
5	316.4	308.9 - 317.6	-3.1	313.3 Unbiased

Tube No. 1 was measured before and after the baseline operating period with a measured loss of 2.3 mils in hot side, tube wall thickness. Unfortunately, the sandblasting necessary to clean the ash and slag coating off the tube so that base metal is reached (for accurately measuring metal thickness) may remove a protective coating resulting in greater than normal metal loss, thus producing biased results on tube 1. However, note that on 10/76 tube 5 was measured a short distance above and below the initially measured spot. The average of the "above" and "below" measurements will provide an unbiased estimate of the after center point, while the initial measured center spot is also an unbiased measurement. The single and double measurements were paired (random order within pairs) across each level of the left and right side walls, thus about 1/2 of the measured differences in tube wall thicknesses will be completely unbiased. The loss of precision through estimating the center "after" measurements was analyzed using the initial panel measurements in the laboratory and found to be very small. The statistical analysis of the baseline operating period will be discussed first, followed by the statistical analysis of the "low NO_x" operating period.

Table 3-20 presents a statistical analysis of possible corrosion measurement bias caused by sandblasting tubes covering the 5 month baseline operating period (5/76 to 10/76). The average change in wall thickness (mils) and number of measurements used in each average are presented for each level measured on the left and right sidewalls. The unbiased and possible biased measurements were obtained as described above. Levels 1, 2, and 6 are separated from levels 3, 4 and 5 so that possible differences due to furnace location can be easily seen. The sample statistics: $\bar{\Delta}$, difference between averages; s_p, pooled

TABLE 3-20

STATISTICAL ANALYSIS OF POSSIBLE BIAS CAUSED BY SANDBLASTING TUBES

(Baseline Operating Period 5/76 to 10/76)

Sidewall and Level Measured	Change in Wall Thickness - Mils				Difference Between Averages	Pooled Standard Error	Students "t"	Degrees of Freedom
	Unbiased Measurements		Possible Biased Measurements					
Left	Average	No.	Average	No.	$\bar{\Delta}$	S_p	t_{up}	n
1	+0.42	12	-2.20	13	-2.62	5.60	-1.17	23
2	-1.26	21	-0.94	19	+0.32	3.67	+0.28	38
6			(+2.22	5)				
3	+1.29	8	-1.00	8	-2.29	4.05	-1.13	14
4	-1.51	9	+1.60	9	+3.11	5.34	+1.24	16
5	-0.81	9	-4.00	10	-3.19	3.60	-1.93 (2)	17
Total	-0.37	59	-1.31	59	-0.93	2.63(1)	-0.79(1)	4(1)
Right								
1	-3.21	16	-8.21	14	-5.00	6.45	-2.12(3)	28
2	-4.08	18	-1.91	17	+2.17	5.18	+1.24	33
6	-2.06	7	-2.23	6	-0.17	5.94	-0.05	11
3	-3.63	6	-4.32	8	-0.69	5.02	-0.25	12
4	-1.98	10	+1.27	11	+3.25	5.93	+1.47	19
5	-6.00	7	-2.40	10	+3.60	3.70	+1.97(2)	15
Total	-3.49	64	-2.97	66	+0.53	3.23(1)	-0.40(1)	5(1)
Grand Total	-1.99	123	-2.19	125	-0.20	3.18(1)	-0.53(1)	10(1)

Notes:

(1) Calculated as paired "t" test of level averages.
(2) Significant at the 10% probability level.
(3) Significant at the 5% probability level.

standard error; t_{up}, students unpaired t; and n, the degrees of freedom associated with each "t" are presented for each level measured on both left and right sidewalls. Paired student "t" tests results are also shown for the left sidewall, right sidewall and combiner; t_{up}, students unpaired "t" and n, the degrees freedom associated with each "t" are presented for each level measured on both left and right sidewalls. Paired student "t" tests results are also shown for the left sidewall, right sidewall and combined sidewalls. Of the 14 "t" tests shown only one is statistically significant at the 5% probability level. Since one statistically significant (5% level) "t" test is expected for 20 "t" tests where no real difference exists, the occurrence of 1 in 14 does not indicate evidence of real bias. The average difference between 123 unbiased measured tube wall thickness changes and 125 possible biased measured tube wall thickness changes is -0.2 mil.

Table 3-21 is identical in form to Table 3-20. However, in Table 3-21 all extreme unbiased or possible biased individual changes in wall thickness (greater than +9.9 mils or less than -9.9 mils) were eliminated from the analysis in Table 3-20. 20 of the 248 (or 8%) wall tube thickness changes were eliminated. The conclusions reached are the same as from Table 3-20. There is no statistical evidence of biased corrosion measurements caused by sandblasting tubes. The average difference between unbiased and possibly biased changes in tube wall thickness of the 228 remaining differences is only -0.07 mils.

The analysis of unbiased vs. possibly biased wall tube thickness measurements for the "low NO_x" operating period is based upon the same principles described above, but it differs in detail as shown below. Table 3-22 presents the 3rd and 4th measurements made on 11/77 and 4/78 respectively on tubes No. 1 and 5 on level 1 of the left sidewall.

Δ_1 combines both unbiased and possibly biased results. For example, the top and bottom fourth measurements of tube number one are possibly biased due to the sandblasting of the top and bottom third measurements. Likewise the center fourth measurement of tube number 5 is possibly biased because of the sandblasting to obtain the center third measurement. Both unbiased and possibly biased measurements can be obtained from each of these tubes as listed in Table 3-22. For tube number 1, the unbiased measurement of -0.7 is obtained by subtracting the average of the third top and bottom measurements from the center fourth measurement while the possibly biased measurement is obtained by subtracting the average of the top and bottom third measurements from the average of the top and bottom fourth measurements. For tube number 5 the unbiased measurement is obtained by subtracting the third center measurement (here the two measurements made for quality control purposes were averaged)

TABLE 3-21

STATISTICAL ANALYSIS OF POSSIBLE BIAS CAUSED BY SANDBLASTING TUBES
(Baseline Operating Period, 5/76 to 10/76 - Screened Data)

Level Measured	Change in Tube Wall Thickness - Mils				Difference Between Averages	Pooled Standard Error	Students "t"	Degrees of Freedom
	Unbiased Measurements		Possibly Biased Measurements					
Left Sidewall	Average	No.	Average	No.	Δ	Sp	t_{up}	n
1	+0.32	10	-1.20	12	-1.52	4.48	-0.79	20
2	-0.74	20	-0.94	19	-0.20	3.27	-0.19	37
6			(+2.22	5)				
3	+1.29	8	-1.00	8	-2.29	4.05	-1.13	14
4	-0.40	8	+1.59	9	+1.99	4.95	+0.83	15
5	-0.81	9	-2.36	8	-1.55	2.64	-1.21	15
Total	-0.07	55	-0.78	61	-0.71	1.69(1)	-0.945(1)	4(1)
Right Sidewall								
1	-1.65	14	-2.79	7	-1.14	4.85	-0.51	19
2	-3.09	16	-0.65	15	+2.44	4.31	+1.57	29
6	-2.06	7	-0.60	5	+1.46	5.95	-2.06(2)	10
3	-2.10	5	-4.32	8	-2.22	4.59	-0.85	11
4	+0.34	8	+0.13	11	-0.21	5.16	-0.09	17
5	-5.00	6	-2.40	10	+2.50	3.43	+1.47	14
Total	-2.26	56	-1.77	56	+0.49	1.98(1)	-0.60(1)	5(1)
Grand Total	-1.17	111	-1.25	117	-0.07	1.87(1)	-0.10(1)	10(1)

Notes:

(1) Calculated by paired t-test of level averages.
(2) Significant at the 10% probability level.

TABLE 3-22

TUBEWALL THICKNESS MEASUREMENTS - MILS

Tube Number	Third Measurement 11/77	(4-3) Δ_1	Fourth Measurement 4/78	B Possibly Biased	U Unbiased	B-U Δ_2
1	314.2 - 316.5 318.8	-1.9	314.6 315.8 314.6 313.3	-2.6	-0.7	-1.8
5	- 313.0 312.8 312.5 -	-1.0	310.8 307.2 311.8 314.4	-5.6	-0.2	-5.4

from the average of the third top and bottom measurements. Δ_2 is simply the possibly biased measurement minus the unbiased measurement. It should be noted that Δ_2 for tube number 1 can be calculated directly from the fourth measurements by subtracting the center measurement from the average of the top and bottom measurements. While for tube number 5, Δ_2 can be calculated directly by subtracting the average of the top and bottom measurements from the center measurement.

Now, let us examine what the expected level of Δ_2 will be assuming that sandblasting for the third measurement does cause increased corrosion. For tubes measured similar to tube number 1 (top and bottom third measurements), the biased measurement should be smaller than the unbiased measurement and Δ_2 should be negative. For tubes measured similar to tube number 5 (center third measurement), the biased measurement should also be smaller than the unbiased measurement and Δ_2 should also be negative. (Note that the fourth center measurement subtracted from the average of top and bottom would be positive.) If there are no third measurements, all three of the fourth top, center and bottom measurements should be unbiased and Δ_2 calculated by subtracting the center measurement from the average of the top and bottom measurements should average 0 except for random sampling error.

Tables 3-23 and 3-24 summarize the statistical analysis of possible bias caused by sandblasting furnace tubes for ultrasonic measurements considering only the third (11/77) and fourth (4/78) measurements for the "low NO_x" operating period. The statistical data within the body of these tables are calculated from the fourth top, center and bottom measurements made on the left and right sidewalls as:

$$(\text{average}^{*}) - (\text{center}), \qquad \text{or} \qquad \frac{(Xt + Xb)}{2} - Xc$$

Thus, for the points where the third measurements were made on the top and bottom, the expected bias direction is negative. If the third measurements were made at the center, the expected bias direction is positive and finally if no third measurements (or all three) were made, the expected bias is zero, assuming always that sandblasting increases corrosion.

---

*top and bottom

TABLE 3-23

STATISTICAL ANALYSIS OF SANDBLAST VS. NON-SANDBLAST MEASUREMENTS

(Left Sidewall Measurements $\left[\frac{(X_T + X_B)}{2} - X_C\right]$ Made on 4/78)

Measurement Pattern 11/77 4/78	Expected Bias	Statis-tics	Level Measured						Total (Weighted)
			1	2	3	4	5	6	
I		$\bar{x}$	+1.263	+0.819	+0.483	+0.600	+2.700	+0.444	+0.860
X $X_T(-)$		s	3.52	2.13	3.05	5.15	3.18	2.37	3.44
- To $X_C(0)$	-	n	40	42	36	17	11	9	156
X $X_B(-)$		t(+)	+2.27**	+1.70	+0.95	+0.48	+2.82**	+0.56	+3.12***
II		$\bar{x}$	+0.312	-0.336	+1.983	-0.925	+3.233	-1.20	+0.360
- X(0)		s	4.12	2.49	5.23	3.03	2.76	0.71	3.70
X To X(-)	+	n	16	20	12	8	3	2	61
- X(0)		t(+)	+0.30	-0.60	+1.31	-0.86	+2.03	2.40	+0.76
III		$\bar{x}$	-0.60	-2.43	+1.03	-0.67	-0.944	-0.55	-0.929
- X(0)		s	3.46	3.40	1.42	1.40	3.22	1.88	2.80
- To X(0)	0	n	5	3	3	3	16	10	40
- X(0)		t(+)	-0.39	-1.24	+1.24	-0.83	+1.17	-0.925	-2.10**

(+) Unpaired "t" test for testing individual level-expected bias cells against $\mu = o$.
* Significant at 10% probability level.
** Significant at 5% probability level.
*** Significant at 1% probability level.

TABLE 3-24

STATISTICAL ANALYSIS OF POSSIBLE BIAS CAUSED BY SANDBLASTING TUBES

(Right Sidewall Measurements $\left[\frac{(X_T + X_B)}{2} - X_M\right]$ Made on 4/78)

Measurement Pattern 11/77 4/78	Expected Bias	Statis- tics	Level Measured						Total (Weighted)
			1	2	3	4	5	6	
I	-	$\bar{x}$	+1.108	-1.082	+0.837	+0.638	+1.142	-0.117	+0.448
X $X_T(-)$		s	2.65	2.98	4.32	3.33	3.22	3.48	3.47
- To $X_C(0)$		n	24	34	46	29	33	18	184
X $X_B(-)$		t	+2.05*	-2.12**	+1.31	+1.09	+2.04**	-0.14	+1.75*
II	+	$\bar{x}$	+0.427	+0.225	-1.800	+2.138	+1.986	+1.50	+0.723
- To $X_T(0)$		s	2.52	2.55	4.58	2.15	4.262	4.20	3.258
X $X_C(-)$		n	11	16	6	8	7	8	56
- $X_B(0)$		t	+0.53	+0.35	-0.96	+2.81**	+1.23	+0.10	+1.66
III	0	$\bar{x}$	+0.352	+1.543	-1.100	-0.100	-0.300	+8.00	+0.300
- $X_T(0)$		s	2.70	2.28	3.72	2.48	2.98	-	2.870
- To $X_C(0)$		n	23	7	9	5	5	1	50
- $X_B(0)$		t	+0.62	+1.79	-0.89	-0.09	-0.23	-	0.74

*Significant at the 10% probability level.
**Significant at the 5% probability level.

Tables 3-23 and 3-24 summarize the statistical analysis of possible bias caused by sandblasting considering only the third and fourth measurements. Examining Table 3-23, it is immediately seen that the average left wall measurement pattern I $\begin{pmatrix} x & & x \\ - & \text{to} & x \\ x & & x \end{pmatrix}$ has a statistically significant positive value of + 0.86 mils instead of the expected negative bias. Also, the average left sidewall measurement pattern III $\begin{pmatrix} - & & x \\ - & \text{to} & x \\ - & & x \end{pmatrix}$ has a statistically significant negative value of -0.93 instead of the zero bias expected. The measurement pattern II $\begin{pmatrix} & & x \\ x & \text{to} & x \\ & & x \end{pmatrix}$ shows no averages that differ significantly from zero.

Table 3-24 for the right sidewall does not have any measurement pattern averages that are statistically significant at the 5% probability level for the entire wall, although measurement pattern I is significant at the 10% probability level. Measurement pattern II produced an average that is significant at the 5% probability level for the fourth level measured but just misses statistical significance at the 10% probability level for the entire wall. Combining the results from the left and the right walls, we obtain the following averages (and number of data sets) for the three measurements patterns $\begin{pmatrix} x & & x \\ - & \text{to} & x \\ x & & x \end{pmatrix}$, $\begin{pmatrix} & & x \\ x & \text{to} & x \\ & & x \end{pmatrix}$ and $\begin{pmatrix} - & & x \\ - & \text{to} & x \\ - & & x \end{pmatrix}$, respectively; + 0.637 (340), + 0.534 (117) and -0.247 (90). The first pattern results are significantly higher than zero at the 1% probability level while the second pattern is significantly greater than zero at the 10% probability level. Combining all of the 547 measurement sets produces an average of +0.469 mils which is significantly greater than zero at the 1% probability level.

These results differ greatly from what would be expected from general engineering experience. There is no ready explanation of why the center tube wall thickness measurement averages about one half of a mill (0.469 mils) smaller than the average of the top and bottom measurements, except for the measurement pattern III, $\begin{pmatrix} & & x \\ x & \text{to} & x \\ & & x \end{pmatrix}$. It is also difficult to explain why the sandblast and measurement pattern I, $\begin{pmatrix} x & & x \\ - & \text{to} & x \\ x & & x \end{pmatrix}$ results in significantly smaller center wall tube thickness measurements than the average top and bottom final measurements. Most engineering experience has shown that cleaning wall surfaces to base metal before exposure leads to increased corrosion and therefore the top and bottom fourth measurements would be expected to average lower than the center spot which was not sandblasted on the third measurement. However, there is one assumption that the above analysis is based on, that may not hold. That assumption is that the first and second measurements made prior to the third measurements had no carryover effect that would influence the final tube wall thickness measurements. This assumption seemed to be valid since the baseline operating period (first and second measurements) showed no generally significant bias due to sandblasting. To check this assumption completely, it will be necessary to analyze the final measurements based upon the sandblasting and measurement patterns for all three prior measurements. This analysis was completed and will be discussed next.

Tables 3-25 and 3-26 present a statistical analysis of possible bias caused by sandblasting tubes for the predominant measurement patterns used on the left and right sidewalls respecively. The body of these tables present the same four statistics $\bar{x}$, s, n and t) as Tables 3-23 and 3-24. These statistics are calculated from the final measurement data of 4/78, average of top and bottom measurement less the center measurement. The measurement patterns are shown in symbolic form in the left column of each table. For example, pattern A indicates that the first two measurements were on the center spot, while the third measurement consisted of top and bottom measurements. A dash, -, indicates no sandblast or measurement. The expected bias assuming sandblasting increases corrosion, is shown in the second column. For pattern A, the expected bias of $\frac{(x_T + x_B)}{2} - x_C$ is positive since the center spot has been sandblasted twice prior to the fourth measurement while the adjacent top and bottom spots were only sandblasted once. In addition, the center spot has had more time for corrosion loss after sandblasting than the top and bottom spots. Similar reasoning leads to determining the expected bias in the other patterns.

Table 3-25 does explain the unexpected results found in Table 3-23. Pattern I of table 3-23 has now been split into patterns A and C on Table 3-25. The expected bias of the fourth measurement considering the three prior measurements is now + (pattern A) and 0 (pattern C) instead of - based only on the prior third measurements. Pattern A produced + averages at all measurement levels and the average of the entire wall is significantly greater than 0 at the 0.1% probability level. Patterns B, and C produced wall averages that were + as expected but were not statistically significantly greater than zero. Pattern C with an expected bias of zero averaged +0.20 mils which is not significantly greater than zero.

TABLE 3-25

STATISTICAL ANALYSIS OF POSSIBLE BIAS CAUSED BY SANDBLASTING TUBES

(Left Sidewall Measurements $\left[\frac{(X_T + X_B)}{2} - X_C\right]$ Made on 4/78)

Measurement Patterns	Expected Bias	Statistics (+)	Level Measured						Total (Weighted)
			1	2	3	4	5	6	
A X X X X – X X X	+	$\bar{x}$	+1.69	+0.98	+3.40	+4.51	+3.08	+0.50	+2.06
		s	3.28	3.22	2.74	2.05	1.49	2.97	2.97
		n	15	19	6	7	4	2	53
		t	+1.99*	+1.33	+3.04**	+5.28***	4.16**	+0.24	5.05***
B X X X – X X X X	+	$\bar{x}$	+0.72	-0.73	+2.45	-0.80	+3.23	-1.7	+0.26
		s	3.74	2.20	3.26	3.25	2.76	–	3.00
		n	13	19	6	7	3	1	49
		t	+0.70	-1.45	+1.84	-0.65	+2.03	–	+0.61
C X X X – – X X X	0	$\bar{x}$	+1.45	+0.93	-0.51	-2.15	+0.32	+0.26	+0.20
		s	3.53	3.14	3.46	4.62	2.98	2.52	3.47
		n	23	21	28	11	8	7	98
		t	+1.96*	+1.36	-0.78	-1.54	+0.30	+0.27	+0.56
D X X – – X X	+	$\bar{x}$	-0.60	-1.5	+0.04	-2.0	+1.00	-0.15	+0.15
		s	3.45	–	3.83	–	4.47	2.33	3.71
		n	5	1	7	1	8	6	28
		t	-0.37	–	+0.03	–	+0.63	t = -0.16	+0.22

(+) Statistics:
$\bar{x}$ - Average
s - Sample standard deviation
n - Number of values included in calculating average
t - Students "t" test, $t = (\bar{x}-o)\sqrt{n}/s$

Significance levels of "t" - *-10%; **-5%, ***-1% probability.

TABLE 3-26

STATISTICAL ANALYSIS OF POSSIBLE BIAS CAUSED BY SANDBLASTING TUBES

(Right Sidewall Measurements $\left[\frac{(X_T + X_B)}{2} - X_C\right]$ Made on 4/78)

Measurement Patterns	Expected Bias	Statistics (*)	Level Measured						Total (Weighted)
			1	2	3	4	5	6	
A X X X X - X X X	+	$\bar{x}$ s n t	+0.92 2.90 12 +1.10	-1.34 2.81 17 -1.97*	+0.51 4.23 7 +0.32	+0.26 3.33 7 +0.21	+1.28 2.93 10 +1.38	-2.40 3.92 6 -1.50	-0.14 3.21 59 -0.32
B X X X - X X X X	+	$\bar{x}$ s n t	+0.19 2.52 12 +0.26	+1.39 3.14 17 +1.83*	-0.13 4.89 3 -0.05	+0.76 3.89 8 +0.55	+0.64 4.32 5 +0.33	-0.09 3.99 9 -0.07	+0.63 3.49 54 +1.33
X X C X - - X X X or X X X - - X X X	0	$\bar{x}$ s n t	+0.28 2.72 17 +0.42	-1.07 3.71 20 -1.29	+0.38 4.54 40 +0.52	+1.10 2.92 10 +1.19	+0.31 3.21 11 +0.32	+0.49 3.08 10 +0.50	+0.12 3.77 108 +0.34
D X X - - X X	+	$\bar{x}$ s n t	+0.72 2.41 9 +0.90	-0.50 .35 2 -2.02	-1.82 0.48 4 -7.58***	-2.0 - 1 -	-2.0 4.24 2 -0.67		-0.33 2.24 18 -0.63
E X X X - X X	+	$\bar{x}$ s n t	+2.29 2.36 7 +2.56**	+0.80 2.82 2 +0.40	-2.30 8.77 2 -0.37	-2.05 0.35 2 -8.28***	-0.6 - 1 -		+0.60 3.63 14 +0.61
F X X - - - X X X	-	$\bar{x}$ s n t	-1.80 1.98 2 -1.29	+2.30 3.39 2 +0.96	+4.80 - 1 -	+0.05 4.09 14 +0.05	+1.92 3.25 15 +2.29**		+1.04 3.62 34 +1.67

See Table 3-25 for explanation of asterisks.

Table 3-26, containing data for the right sidewall had no pattern averages for the entire wall that were statistically significant at the 10% (or smaller) probability level. The average value of $\frac{(x_T + x_B)}{2} - x_C$ for all measurements of both the left and right sidewalls are + 0.56 and + 0.16 for expected + and 0 biases respectively. Thus, it can be concluded there is a slight bias of about one-half of a mill over a 17 month exposure period due to sandblasting. (95% confidence limits are 0.2 to 0.9 mils). Although the left side wall exhibited more bias due to sandblasting than the right wall, there appears to be no consistent change in bias due to furnace level measured such as within the burner level vs. outside the burner level.

The third and fourth questions that the measurement program was designed to answer will be addressed next: (3) Are corrosion rates of fireside, furnace tube walls different at different furnace locations when exposed to (a) baseline operation and (b) staged combustion for "low NO_x" operation? (4) Are corrosion rates higher under "low NO_x" operation than under baseline operation? Does this difference if any depend upon furnace location, i.e., side vs. burner walls, within or outside burner elevation, etc.?

Experience and engineering judgment indicate that external corrosion of boiler tubes will vary throughout the inside of the furnace since temperatures, slagging patterns and gaseous composition vary considerably over each furnace wall. It would be desirable to analyze the ultrasonic measurements for small portions of each wall. However, this is not feasible unless the precision of the measurement process (calibration, measurement and tube-to-tube variation included) and the number of measurements are of adequate size. In this study the smallest area practical for statistical analysis is one half of a wall.

STATISTICAL ANALYSIS OF ULTRASONIC DATA

To assess the statistical significance of the wall or half-wall average tube wall thickness change, the most appropriate "error term" is calculated from the differences between level averages within burner walls. Instrument calibrations were not made more frequently than once per level measured. The levels were far enough apart to expect different corrosion rates and the spots to be measured were determined at each level independently.

This approach does not bias our analysis if calibration errors are insignificant. Comparisons between level means provide a proper error term. Our only loss if calibration variance is negligible is a slight loss of sensitivity due to a reduced number of degrees of freedom. However, experience has shown that calibration variance appears to be far from negligible.

Table 3-27 contains a summary of the furnace wall tube hot side metal thickness changes (mils) for the baseline operation (5 months) and low NO_x operation (12 month duration). The body of the table presents the average thickness change for each of the six measurement levels of each furnace wall. Table 3-28 is identical to Table 3-27 except that the 5 month baseline operation data has been converted to a mils/year basis for ready comparison with the 12 month "low-NO_x" operation data. The averages have been calculated from all of the paired data (before and after measurements) available for each level after screening out obvious outline data (20 out of 974 differences). The weighted averages ($\bar{X}$), number of differences (n) and pooled standard deviations(s) are shown for half-walls (burner and nonburner areas), walls and the whole furnace for both the baseline and low-NO_x operating periods. Individual wall level averages vary from a high loss of -8.26 mils (left wall, middle burner level under low NO_x operation) to a gain of 0.81 mils (right wall, level 1 at 27 feet above top burners under low-NO_x operation). These data will be analyzed by Shewhart Control Charts and the calculation of 95% confidence limits (by classical and successive difference methods).

Figure 3-7 presents $\bar{X}$ (average) and R (range) Shewart control charts of the half-wall data from Table 3-27. Half-wall averages and ranges are plotted for all four walls under both baseline and low-NO_x operation. Two and three sigma control limits are shown to estimate the 95 and 99.7% probability limits for individual plotted points. The individual ranges calculated from the high and low values of each half-wall are all within statistical control and provide estimates of the standard deviation, $\sigma = 1.54$ and 1.43 mils (level mean variation) respectively for baseline and low NO_x operation. The average furnace tube wall thickness loss was 2.18 mils during baseline operation. All of the half-wall averages were within the 3σ control limit, but the right nonburner half-wall had an average loss of 4.40 mils which is outside of the lower 2σ control limit (3.96) for half-wall averages.

The furnace average tube wall thickness loss during low NO_x operation was 3.43 mils. However, two of the half-wall averages were outside of the 3σ (97.3% probability) control limits; left wall, burner area (-6.24 mils) and right wall nonburner area (+0.36 mils). In addition, the right side wall, burner area average of -5.29 mils is outside of the lower 2σ limit of -5.10 mils. Our tentative conclusions from the control chart analysis are:

TABLE 3-27

WALL TUBE HOT SIDE METAL THICKNESS CHANGES:MILS:
(BY ULTRASONIC MEASUREMENTS)
(PAIRED DATA)

Level Measured Relative to Burners	Baseline Operation-5 Months					Low NO_x Operation-12 Months				
	Furnace Wall				Furnace Average	Furnace Wall				Furnace Average
	Left	Right	Front	Rear		Left	Right	Front	Rear	
Nonburner Area										
1. 27 Feet Above	-1.51	-5.40	+0.46	-	-3.12	-3.89	+0.81	-2.92	-1.50	-1.94
2. 8 Feet Above	-1.35	-4.44	-2.39	-0.13	-2.36	-4.45	+0.07	-4.04	-4.10	-2.96
6. 13 Feet Below	-0.30	-2.21	-	-3.77	-2.39	-2.48	+0.04	-	+0.21	-0.51
Weighted Average, $\bar{x}$	-1.32	-4.40	-1.35	-1.51	-2.60	-3.94	+0.36	-3.37	-1.84	-2.11
Number, n	73	85	22	29	209	102	94	55	89	340
Standard Deviation, s_p	5.57	6.47	4.59	4.86	5.78	4.71	3.40	3.47	5.43	4.42
Burner Area										
3. Top Burners	+0.73	-3.92	-1.78	-0.62	-1.35	-4.99	-7.14	-4.31	-3.46	-5.48
4. Middle Burners	+0.04	-0.88	-1.79	-1.56	-0.86	-8.26	-3.49	-2.68	-5.11	-4.86
5. Bottom Burners	-2.32	-4.24	-3.04	+0.17	-2.81	-7.17	-2.47	-3.51	-4.13	-4.41
Weighted Average, $\bar{x}$	-0.63	-2.89	-2.17	-0.72	-1.66	-6.24	-5.29	-3.50	-4.17	-5.05
Number, n	54	56	29	29	168	83	91	48	54	276
Standard Deviation, s_p	4.49	5.59	4.80	4.13	4.88	6.77	4.78	3.71	6.00	5.55
Grand Average	-1.03	-3.80	-1.82	-1.12	-2.18	-4.97	-2.42	-3.43	-2.72	-3.43
Number	127	141	51	58	377	185	185	103	143	616
Pooled Standard Dev. s_p	5.14	6.14	4.71	4.51	5.40	5.73	4.14	3.58	5.65	4.96

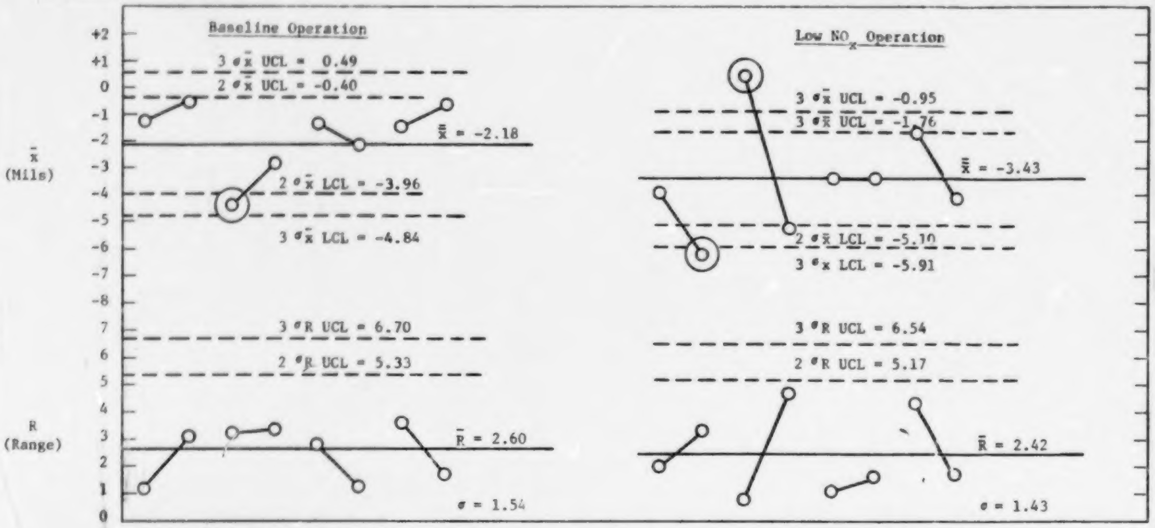
TABLE 3-28

WALL TUBE HOT SIDE METAL THICKNESS CHANGE RATE:MILS/YEAR (By Ultrasonic Measurements)

(Paired Data)

LEVEL MEASURED RELATIVE TO BURNERS		BASELINE OPERATION - 5 MONTHS					"LOW NOx" OPERATION - 12 MONTHS				
		FURNACE WALL					FURNACE WALL				
		LEFT	RIGHT	FRONT	REAR	FURNACE AVERAGE	LEFT	RIGHT	FRONT	REAR	FURNACE AVERAGE
NON BURNER AREA											
1		-3.62	-12.96	+1.10	-	-7.49	-3.89	+0.81	-2.92	-1.50	-1.94
2		-3.24	-10.66	-5.74	-0.31	-5.66	-4.45	+0.07	-4.04	-4.10	-2.96
6		-0.30	- 5.30	-	-9.05	-5.74	-2.48	+0.04	-	+0.21	-0.51
	$\bar{x}$	-3.17	-10.56	-3.24	-3.62	-6.24	-3.94	+0.36	-3.37	1.84	-2.11
	n	73	85	22	29	209	102	94	55	89	340
	Sp	5.57	6.47	4.59	4.86	5.78	4.71	3.40	3.47	5.43	4.42
BURNER AREA											
3		+1.75	- 9.41	-4.27	-1.49	-3.24	-4.99	-7.14	-4.31	-3.46	-5.48
4		+0.10	- 2.11	-4.30	-3.74	-2.06	-8.26	-3.49	-2.68	-5.11	-4.86
5		-5.57	-10.18	-7.30	+0.41	-6.74	-7.17	-2.47	-3.51	-4.13	-4.41
	$\bar{x}$	-1.51	- 6.94	-5.21	-1.73	-3.98	-6.24	-5.29	-3.50	-4.17	-5.05
	n	54	56	29	29	168	83	91	48	54	276
	Sp	4.49	5.59	4.80	4.13	4.88	6.77	4.78	3.71	6.00	5.55
	$\bar{\bar{x}}$	-2.46	- 9.12	-4.36	-2.68	-5.23	-4.97	-2.42	-3.431	-2.72	-3.43
	n	127	141	51	58	377	185	185	103	143	616

Method Ultrasonic	Prod. CRIST No. 7 Boiler		Mach. No.	Period Covered
Characteristic Tube Wall Thickness	Specification Limits	Max.	Min.	Sample Size, Groups of Per
Unit of Measurement Mils (0.001 Inches)	Control Limits	Max.	Min.	Inspector 1 2 3



Identification		Baseline Operation - 5 Months								
Levels*		Left		Right		Front		Rear		
N.B.	B.	N.B.	B.	N.B.	B.	N.B.	B.	N.B.	B.	
1	3	-1.51	+0.73	-5.40	-3.92	+0.46	-1.78	-	-0.62	
2	4	-1.35	+0.04	-4.44	-0.88	-2.39	-1.79	-0.13	-1.56	
6	5	-0.30	-2.32	-2.21	-4.24	-	-3.04	-3.77	+0.17	
Total										
WTD. $\bar{x}$		-1.32	-0.63	-4.40	-2.89	-1.35	-2.17	-1.51	-0.72	$\bar{\bar{x}}$ = -2.18
Largest Value										
Smallest Value										
Range		1.21	3.05	3.19	3.36	2.85	1.26	3.64	1.73	$\bar{R}$ = 2.60
										σ = 1.54

(S = 1.89

*N.B. - Non-Burner Measurement Level

B. - Burner Measurement Level

		"Low NO$_x$" Operation - 12 Months								
Levels		Left		Right		Front		Rear		
N.B.	B.	N.B.	B.	N.B.	B.	N.B.	B.	N.B.	B.	
1	3	-3.89	-4.99	+0.81	-7.14	-2.92	-4.31	-1.50	-3.46	
2	4	-4.45	-8.26	+0.07	-3.49	-4.04	-2.68	-4.10	-5.11	
6	5	-2.48	-7.17	+0.04	-2.47	-	-3.51	+0.21	-4.13	
Total										
WTD. $\bar{x}$		-3.94	-6.24	+0.36	-5.29	-3.37	-3.50	-1.84	-4.17	$\bar{\bar{x}}$ = -3.43
Largest Value										
Smallest Value										
Range		1.97	3.27	0.77	4.67	1.12	1.63	4.31	1.65	$\bar{R}$ = +2.42

N.B. - Non Burner measurements level.
B. - Burner Measurement Level.

Figure 3-7. Shewart Control Charts.

- The variation of measurement level averages within half-walls is uniform within half-walls during both baseline and low NO_x operation and equals about 1.5 mils (σ calculated from average ranges).

- With the possible exception of the right sidewall nonburner average, all of the half-wall averages during the baseline operation are about equal after allowing for random level to level variation.

- The low NO_x operation produced significantly high metal loss within the left wall burner area and possibly, significantly high metal loss within the right wall burner area. The right nonburner area showed significantly less metal loss than the furnace average.

Before calculating 95% confidence limits for the half-wall and full wall average metal losses, there is an apparent negative correlation between the baseline and low-NO_x half-wall averages that could be explained by calibration error and should be analyzed. Note that large positive (negative) deviations from the baseline average loss of 2.18 mils generally produced large negative (positive) deviations from the low-NO_x average loss of -3.43 mils. Table 3-29 presents the data.

TABLE 3-29

CORRELATION OF BASELINE VS LOW-NO_x HALF-WALL AVERAGES

Half-Wall	Weighted Averages Baseline (x)	Weighted Averages Low-NO_x (y)	Predicted Low-NO_x (y')	Predicted Minus Actual (y'-y)
1 Left - Nonburner	-1.32	-3.94	-4.08	-0.14
2 Left - Burner	-0.63	-6.24	-4.81	+1.43
3 Right - Nonburner	-4.40	+0.36	-0.84	-1.20
4 Right - Burner	-2.89	-5.29	-2.43	+2.86
5 Front - Nonburner	-1.35	-3.37	-4.05	-0.68
6 Front - Burner	-2.17	-3.50	-3.19	+0.31
7 Rear - Nonburner	-1.51	-1.84	-3.88	-2.04
8 Rear - Burner	-0.72	-4.17	-4.71	-0.54
Weighted Averages	-2.18	-3.43	-	-
Unweighted Averages	-1.87	-3.50	-3.50	0

The least squares regression equation relating low-NO_x operation half-wall tube wall average thickness changes to the corresponding baseline operation results is $y = 5.47-1.05x$ as shown in Figure 3-8. The coefficient of correlation, $r = -0.65$ is not

- The variation of measurement level averages within half-walls is uniform within half-walls during both baseline and low NO_x operation and equals about 1.5 mils (σ calculated from average ranges).
- With the possible exception of the right sidewall nonburner average, all of the half-wall averages during the baseline operation are about equal after allowing for random level to level variation.
- The low NO_x operation produced significantly high metal loss within the left wall burner area and possibly, significantly high metal loss within the right wall burner area. The right nonburner area showed significantly less metal loss than the furnace average.

Before calculating 95% confidence limits for the half-wall and full wall average metal losses, there is an apparent negative correlation between the baseline and low-NO_x half-wall averages that could be explained by calibration error and should be analyzed. Note that large positive (negative) deviations from the baseline average loss of 2.18 mils generally produced large negative (positive) deviations from the low-NO_x average loss of -3.43 mils. Table 3-29 presents the data.

TABLE 3-29

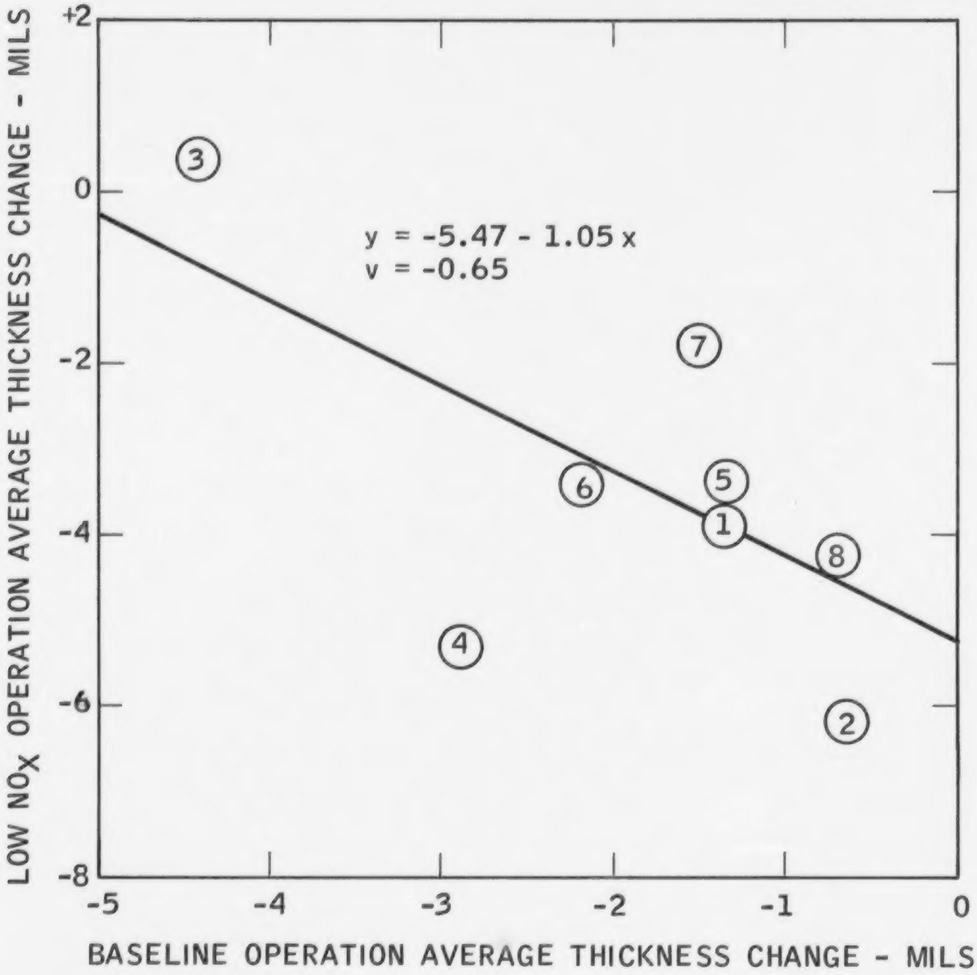
CORRELATION OF BASELINE VS LOW-NO_x HALF-WALL AVERAGES

Half-Wall	Weighted Averages		Predicted	Predicted
	Baseline (x)	Low-NO_x (y)	Low-NO_x (y')	Minus Actual (y'-y)
1 Left - Nonburner	-1.32	-3.94	-4.08	-0.14
2 Left - Burner	-0.63	-6.24	-4.81	+1.43
3 Right - Nonburner	-4.40	+0.36	-0.84	-1.20
4 Right - Burner	-2.89	-5.29	-2.43	+2.86
5 Front - Nonburner	-1.35	-3.37	-4.05	-0.68
6 Front - Burner	-2.17	-3.50	-3.19	+0.31
7 Rear - Nonburner	-1.51	-1.84	-3.88	-2.04
8 Rear - Burner	-0.72	-4.17	-4.71	-0.54
Weighted Averages	-2.18	-3.43	-	-
Unweighted Averages	-1.87	-3.50	-3.50	0

The least squares regression equation relating low-NO_x operation half-wall tube wall average thickness changes to the corresponding baseline operation results is $y = 5.47-1.05x$ as shown in Figure 3-8. The coefficient of correlation, $r = -0.65$ is not

Figure 3-8

BASELINE HALF - WALL AVERAGE THICKNESS CHANGE
LOW NO_X HALF - WALL AVERAGE THICKNESS CHANGE



(Circled numbers refer to data represented in Table 3-29).

quite significant at the 5% probability level. 95% confidence limits calculated from this sample within which the true correlation coefficient should fall are -0.93 to +0.1. Thus, there is insufficient evidence from these data to conclude that this apparent negative relationship is real. However, it may be noted that if we assume that the regression equation is real and due to ultrasonic instrument calibration error, the "corrected" low-NO_x operation half-wall averages y' would all be within 2x limits except the right wall - nonburner area.

CALCULATION OF 95% CONFIDENCE LIMITS

Table 3-30 presents the details for calculating the estimated variance of level averages for the left sidewall of Crist No. 7 furnace during baseline operation. The level "means" (average change in tube wall thickness), first and second differences are shown for the 6 levels measured on the left furnace wall. For example: +0.16 = -1.35 - (-1.51), +2.08 = +0.73 - (-1.35), +1.92 = +2.08 - (+0.16). The calculations in the $\bar{\Delta}$ column are the standard classical methods for determining the mean ($\bar{x}$), variance (s^2) and standard error of the grand mean $s_{\bar{\bar{x}}}$ for a set of numbers. The calculations in the difference columns follows Professor John W. Tukey's (15, 16) method of analyzing the Widows Creek corrosion data. The sums of squares of successive differences are divided by the product of (a) the number of differences squared and (b) the sum of squares of the binomial coefficients when the difference is written out in detail. Thus, for the first two orders of differences, the following coefficients and sums of squares are:

First $(y_{i+1} - y_i)$: +1, -1; $1^2 + 1^2 = 2$

Second $(y_{i+2} - 2y_{i+1} + y_i)$: 1, -2, 1; $1^2 + 2^2 + 1 = 6$

The estimated variance of the six level means are approximately equal: 1:187, 1.264 and 1.211 and for this wall the standard method produces the most appropriate value (1.187) as will be seen when the appropriate degress of freedom are considered.

Table 3-31 presents alternate estimates of the overall variance of measurements (level means within walls) for all four furnace walls of Crist No. 7 boiler under baseline operation calculated as shown in Table 3-30. The estimated variances (s^2) within each column are fairly well clustered around its mean or median value. (The Shewhart Control Chart for ranges also showed no evidence of lack of homogenity within half-walls). Thus, the estimated s_p (standard error of level means within walls) has been calculated from the mean of all four wall variances for use in calculating confidence intervals and limits.

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TABLE 3-30

DETAILED CALCULATIONS FOR LEFT SIDEWALL - BASELINE OPERATION

Level Measured	$\bar{\Delta}$ Average Change in Wall Thickness	First Differences	Second Differences
1	-1.51		
2	-1.35	+0.16	
3	+0,73	+2.08	+1.92
4	+0.04	-0.69	-2.77
5	-2.32	-2.27	-1.58
6	-0.30	+1.63	+3.90
$\bar{x}_1$, Mean	-0.82	+0.18	+0.37
Σx^2, Sum of Squares Divisor	9.97 *	12.638 (5x2=10)**	29.066 (4x6=24)**
s^2, Estimated Variance	1.187	1.264	1.211
$s^2_{\bar{x}}$, Variance/6	0.198	0.211	0.202
$s_{\bar{x}}$, $\sqrt{s^2_{\bar{x}}}$	0.445	0.459	0.449

* $\Sigma(\bar{\Delta})^2 - \frac{(\Sigma\bar{\Delta})^2}{6}$ is divided by 6-1

** (number of squares summed)·(sum of squares of coefficients of differences), i.e., first = $1^2 + 1^2 = 2$, and second = $1^2 + 2^2 + 1^2 = 6$)

Note: The choice of algebraic sign for the differences can be arbitrary, so long as it's consistent.

TABLE 3-31

ALTERNATE ESTIMATES OF OVERALL VARIANCE OF MEASUREMENT (OF LEVEL MEANS) FOR WALLS OF CRIST NO. 7 FURNACE

(Five Month Baseline Operation)

Estimated Variances Based Upon:

Wall	Level Averages	First Differences	Second Differences
Left	1.187	1.264	1.211
Right	2.749	2.653	3.094
Front	1.738	1.257	0.772
Rear	2.523	2.455	2.193
Mean	2.049*	1.907*	1.818*
Median	2.130	1.860	1.702
Estimated S_p	1.431	1.381	1.348
Degrees of Freedom	18	10.3	4.8
$t_{.05}$	2.101	2.228	2.60
$t_{.05/4}$	2.78	3.08	3.81
$t_{.05/8}$	3.09	3.45	4.52
95% Confidence Intervals:			
Half-Walls (3 Levels)			
o Individual	±1.74	±1.78	±2.02
o Simultaneous	±2.55	±2.75	±3.52
Full Walls (6 Levels)			
o Individual	±1.23	±1.26	±1.43
o Simultaneous	±1.62	±1.71	±2.10
Furnace (22 Levels)	+0.64	+0.66	+0.75

* Variance used in calculating estimated s_p, the pooled estimate of within wall standard error of level means. This estimate of overall variance was used in calculating the 95% confidence intervals.

Confidence intervals are calculated from the expression $\pm \frac{ts_p}{\sqrt{n}}$ The value of t depends upon the probability level chosen and the number of degrees of freedom associated with s_p while n equals the number of level means within the average. Both individual and simultaneous confidence limits have been calculated so that the average number of failures of any/all of the collection (for example 4 walls) is 0.05; just as the average number of failures of any one individual confidence interval is 0.05. Thus, for the four wall averages, the simultaneous t value is obtained by using 0.05/4 (not 0.05) as the probability value to use in finding the critical t value.

The number of degrees of freedom to be used with the estimated s_p calculated from the level averages is equal to the number of level means (22) less the number of walls (4). The number of equivalent degrees of freedom for the standard errors estimated from the first and second differences has been obtained from Table 3-32. For example, 10.3 for first differences = (2x2.91) + (2x2.25). Since the confidence intervals calculated from the level averages are shorter than the intervals calculated from the successive difference method, they were used in calculating the 95% confidence limits shown in Table 3-33. Note that the decrease in number of degrees of freedom overcomes the reduced estimates of s_p from the successive difference method.

TABLE 3-32

VALUES OF EQUIVALENT DEGREES OF FREEDOM FOR MEAN SQUARE SUCCESSIVE DIFFERENCES OF ORDERS 1 TO 3 BASED ON 3 TO 6 SUCCESSIVE VALUES

(Based on Morse and Grubbs, 1947)

Number of Values	Order of Successive Differences		
	First	Second	Third
3	1.60	1.00	xxx
4	2.25	1.38	1.00
5	2.91	1.86	1.28
6	3.57	2.36	1.66

Table 3-33 presents individual and simultaneous 95% confidence limits for half-wall, full wall and furnace average tube wall thickness change for the five month baseline operation. On a simultaneous basis, the only half-wall averages showing statistically significant corrosion are the right wall, nonburner and burner areas. The burner area of the front wall is significant on an individual basis but not on a simultaneous basis. (Note that if the control chart limits (Figure 3-7) for averages had

TABLE 3-33

INDIVIDUAL AND SIMULTANEOUS 95% CONFIDENCE LIMITS
(BASELINE OPERATION - MILS)

Area	Average	95% Confidence Limits	
		Individual	Simultaneous
Left Wall	-1.03	-2.26 to +0.20	-2.65 to +0.59
o Nonburner	-1.32	-3.05 to +0.41	-3.87 to +1.23
o Burner	-0.63	-1.86 to +0.60	-3.18 to +1.92
Right Wall	-3.80	-5.03 to -2.57*	-5.42 to -2.18*
o Nonburner	-4.40	-6.13 to -2.67*	-6.95 to -1.85*
o Burner	-2.89	-4.62 to -1.16*	-5.44 to -0.34*
Front Wall	-1.82	-3.16 to -0.48*	-3.60 to -0.04*
o Nonburner	-1.35	-3.48 to -0.78	-4.48 to +1.78
o Burner	-2.17	-3.90 to -0.44*	-4.72 to +0.38
Rear Wall	-1.12	-2.46 to +0.22	-2.90 to +0.66
o Nonburner	-1.51	-3.64 to +0.62	-4.64 to +1.62
o Burner	-0.72	-2.45 to +1.01	-3.27 to +1.83
Furnace	-2.18	-2.82 to -1.54*	-
o Nonburner	-2.60	-3.61 to -1.59*	-3.70 to -1.50*
o Burner	-1.66	-2.53 to -0.79*	-2.66 to -0.66*

* Confidence limits do not include zero; average thickness loss is significantly greater than 0 at the 5% probability level.

been constructed around zero - to test if individual half-walls were significantly different from zero rather than significantly different from the weighted grand mean of -2.18 - the same 3 half-walls would have been outside of the lower 2 sigma limit of -1.78.)

Figure 3-9 is a plot of the 95% simultaneous confidence limits for Crist No. 7 furnace half walls, full walls and entire furnace average tube wall thickness changes during the five month baseline operating period.

The twelve month low-NO_x operating period data from Table 3-27 was analyzed in a similar manner as described above for the five-month baseline operating data. Table 3-34 presents alternate estimates of overall variance of level means based upon level means, first and second successive differences. The 95% confidence intervals calculated from level averages again turned out to be shorter than the intervals calculated for the first or second differences.

Table 3-35 presents the individual and simultaneous 95% confidence limits using the pooled estimate of s_p calculated from the sum of squares of level means. Only the nonburner half-walls of the right and rear walls produced averages which were not statistically significant at the simultaneous 95% confidence limits. Note again, that if the control chart (Figure 3-7) limits for averages had been constructed around zero to test whether individual half-wall averages were significantly different from zero, only the right wall burner average would have been inside of the lower 2 sigma control limit. This agrees with the results in Table 3-35 for individual 95% confidence limitation.

Figure 3-10 is a plot of the 95% simultaneous confidence limit for Crist No. 7 furnace half-walls, full walls and entire furnace average tube wall thickness changes during the twelve month low-NO_x operating period.

The statistical analysis of furnace wall tube corrosion enables us to answer question 3 as follows: under baseline operation, Crist No. 7 furnace experienced significant corrosion rates on only the right side wall. Although the average metal loss of the nonburner area was greater than the burner area, the difference was not statistically significant. For the entire furnace, the average tube wall metal loss was 2.2 mils with 95% confidence limits of 1.5 to 2.8 mil loss.

Under the 12 month low-NO_x operation, Crist No. 7 furnace experienced a significant level of wall tube metal loss on all half-walls except the nonburner areas of the right and rear

Figure 3-9

95% SIMULTANEOUS CONFIDENCE LIMITS - CRIST NO. 7 FURNACE HALF AND FULL WALLS
(5 MONTH BASELINE OPERATION)

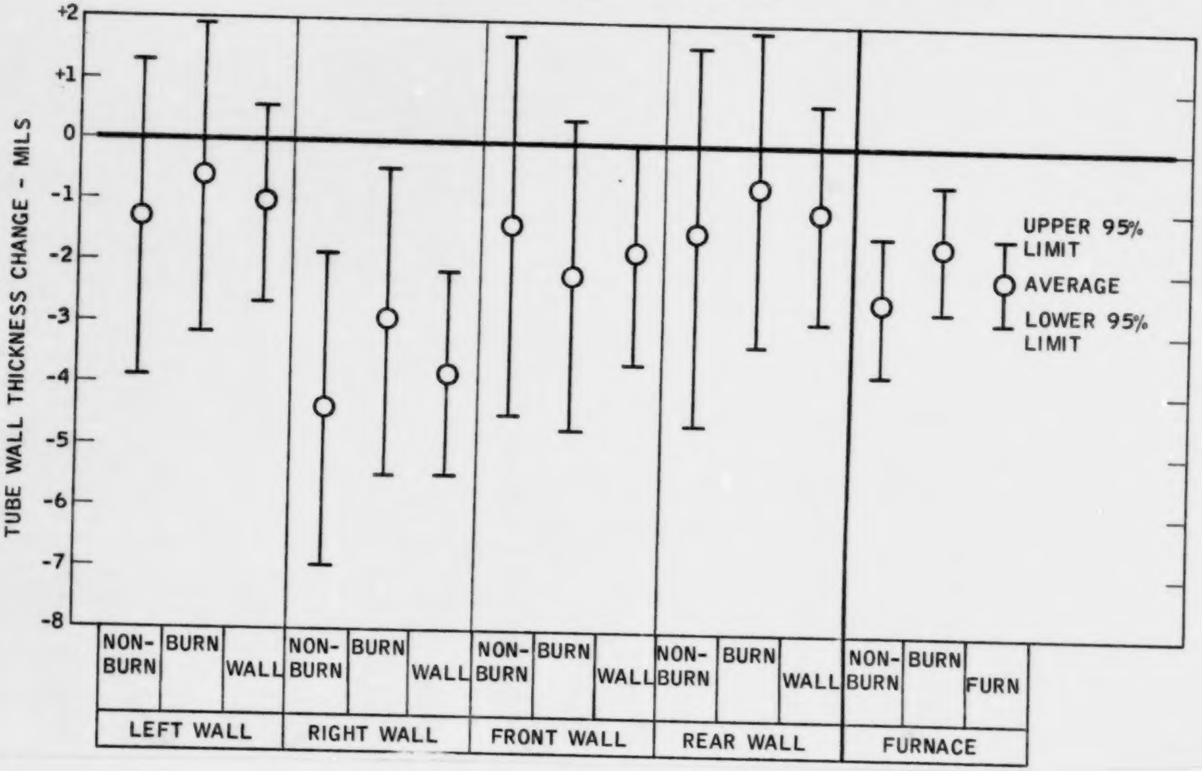

TABLE 3-34

ALTERNATE ESTIMATE OF OVERALL VARIANCE OF MEASUREMENTS (OF LEVEL MEANS) FOR WALLS OF CRIST NO. 7 FURNACE, LOW NO_x OPERATION

Wall	Estimates Based Upon: Level Averages	First Differences	Second Differences
Left	2.143	3.448	1.643
Right	3.007	7.309	7.037
Front	0.699	0.584	0.577
Rear	1.985	2.969	1.415
Mean	1.959*	3.578*	2.668
Median	2.064	3.208	1.529*
Estimated s_p	1.400	1.891	1.237
Degrees of Freedom	19	11	5
t.05	2.09	2.20	2.57
t.05/4	2.76	2.98	3.81
t.05/8	3.07	3.36	4.52
95% Confidence Intervals:			
• 1/2 Walls (3 levels)			
• Individual	±1.69	±2.40	±1.84
• Simultaneous	±2.48	±3.67	±3.23
• Full Walls (6 Levels)			
+ Individual	±1.19	±1.70	±1.30
+ Simultaneous	±1.58	±2.30	±1.92
• Furnace (23 Levels)	±0.61	±0.87	±0.66

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* This estimate of over-all variance was used in calculating the 95% confidence intervals.

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TABLE 3-35

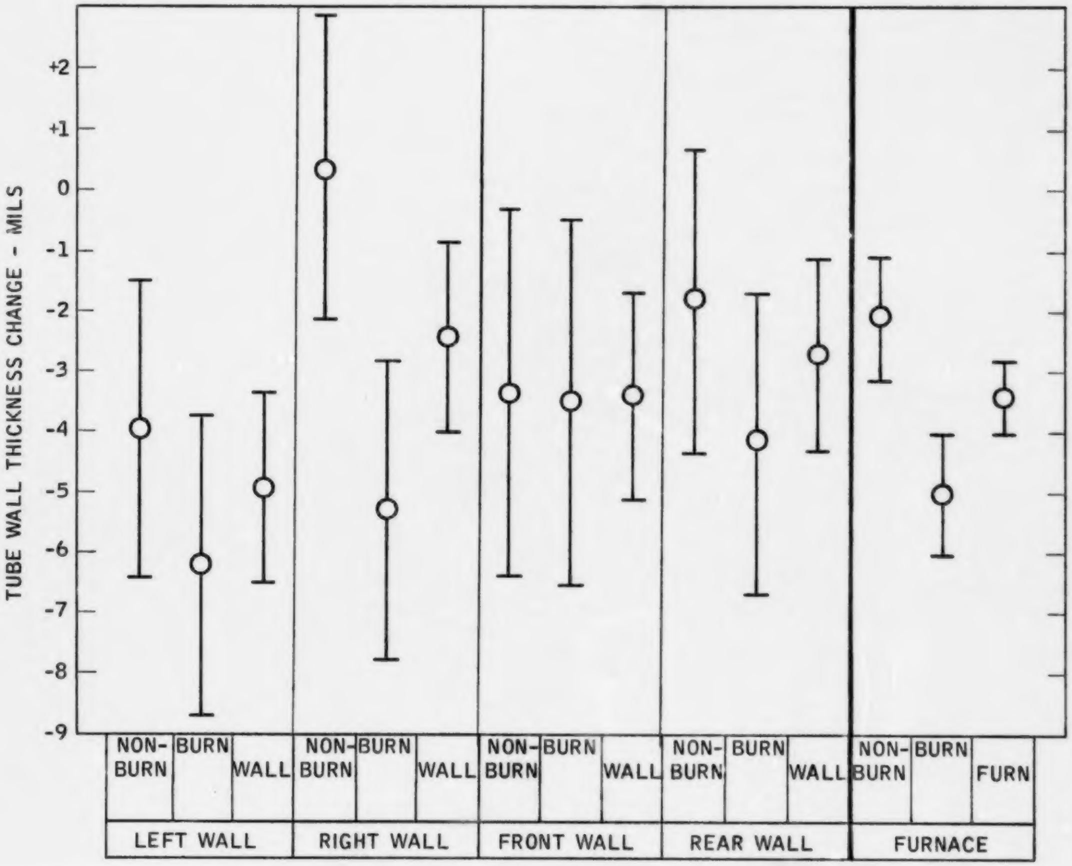
INDIVIDUAL AND SIMULTANEOUS 95% CONFIDENCE LIMITS (LOW NO_x OPERATION - MILS OR MILS PER YEAR)

Area	Weighted Average	95% Confidence Limits	
		Individual	Simultaneous
Left Wall	-4.97	-6.16 to -3.78*	-6.55 to -3.39*
o Nonburner	-3.94	-5.63 to -2.25*	-6.42 to -1.46*
o Burner	-6.24	-7.93 to -4.55*	-8.72 to -3.76*
Right Wall	-2.42	-3.61 to -1.23*	-4.00 to -0.84*
o Nonburer	+0.36	-1.33 to +2.05	-2.12 to +2.84
o Burner	-5.29	-6.98 to -3.60*	-7.77 to -2.81*
Front Wall	-3.43	-4.74 to -2.12*	-5.16 to -1.70*
o Nonburner	-3.37	-5.43 to -1.31*	-6.41 to -0.33*
o Burner	-3.50	-5.56 to -1.44*	-6.54 to -0.46*
Rear Wall	-2.72	-3.91 to -1.53*	-4.30 to -1.14*
o Nonburner	-1.84	-3.53 to -0.15*	-4.32 to +0.64
o Burner	-4.17	-5.86 to -1.48*	-6.65 to -1.69*
Furnace	-3.43	-4.04 to -2-82*	-4.04 to 2.82*
o Nonburner	-2.11	-2.99 to -1.23*	3.13 to -1.09*
o Burner	-5.05	-5.89 to -4.21*	-6.03 to -4.07*

* Confidence limits do not include zero, indicating that the average wall thickness loss is significantly greater than zero at the 5% probability level.

Figure 3-10

95% SIMULTANEOUS CONFIDENCE LIMITS - CRIST NO.7 FURNACE HALF AND FULL WALLS
(12 MONTH LOW NOX OPERATION)



walls. For the furnace as a whole, the average metal loss on burner zone was 5.05 mils which was statistically, significantly higher than the average of 2.11 mils loss of the nonburner zone. The nonburner area of the left wall experienced significantly higher metal loss than the nonburner area of the right wall during the low-NO_x operating period, just the reverse of the baseline operating period. No explanation could be found for this phenomenon except the possibility of miscalibration of the ultrasonic instrument following the baseline operation. The low-NO_x corrosion data was obtained by measuring the furnace wall thickness before, after, and two-thirds of the way through the 12 month low-NO_x operating period. In this report, only the "before-vs-after" results are reported. However, the boiler's manufacturer (FWEC) has pointed out that when the intermediate measurements are considered, (in Appendix H) significant wall corrosion occurred only during the first portion of the period.

COMPARISON OF BASELINE AND LOW-NO_x LOSS DATA

Table 3-36 presents a comparison of five month baseline and 12 month low-NO_x furnace tube wall thickness loss data. Column 1 lists the non-burner and burner average loss for each furnace wall (mils, mils per year and mils per $\sqrt{year}$) for the 12 month low-NO_x operating period. Columns 2, 3 and 4 list the corresponding loss data for the 5 month baseline operating period-mils, mils per year and mils per $\sqrt{year}$, respectively, for comparison purposes. Since the right wall, nonburner area results are so disparate from the rest of the data (see Figure 3-7), the nonburner grand average has been calculated with and without the right wall results. 95% confidence limits for the low-NO_x operation nonburner (less right wall) and burner grand averages are also shown in Table 3-36.

The baseline and low-NO_x loss data for both nonburner and burner furnace area can be compared on three different bases: mils, mils per year and mils per $\sqrt{year}$. (Other bases could be used but these three seem adequate considering the state of present knowledge of coal-fired, hot side furnace tube corrosion.) Since the comparison using mil loss data is obviously biased in favor of the baseline operation (because of the difference in exposure times), no importance can be attached to its statistically significant difference. Omitting the right wall, nonburner area averages, all 7 of the half wall low-NO_x averages produced larger metal losses than the corresponding baseline averages calculated as mils.

However, both the mils per year (equal loss per unit of time) and mils per year (decreasing rate of loss with time) can provide valid comparisons. On a mil per $\sqrt{year}$ basis, four of the seven half-wall comparisons produced lower baseline loss than

TABLE 3-36

COMPARISON OF 5-MONTH BASELINE AND 12-MONTH LOW NO_x AVERAGE TUBEWALL THICKNESS LOSS DATA (BY ULTRASONIC MEASUREMENT)

Area	Low NO_x Mils, Mil/Year or Mil/ $\sqrt{\text{Year}}$	Baseline Mils / 5 Months	Mils / Year	Mils/ $\sqrt{\text{Year}}$
Nonburner:				
Left Wall	-3.94	-1.32	-3.17	-2.04
Right Wall	+0.36	-4.40	-10.56	-6.82
Front Wall	-3.37	-1.35	-3.24	-2.09
Rear Wall	-1.84	-1.51	-3.62	-2.34
Total	-2.11	-2.60	-6.25	-4.03
Less Right Wall	-3.05	-1.37	-3.30	-2.12
	-4.6 to -1.5 95% simultaneous confidence limits			
Burner:				
Left Wall	-6.24	-0.063	-1.51	-0.98
Right Wall	-5.29	-2.89	-6.94	-4.48
Front Wall	-3.50	-2.17	-5.21	-3.36
Rear Wall	-4.17	-0.72	-1.73	-1.12
Total	-5.05	-1.66	-4.00	-2.58
	-6.0 to -4.1 95% simultaneous confidence limits			

low-NO_x loss and the overall average difference is not statistically significant. However, it should be noted that the baseline operation average of 4.0 mil/year loss for the overall burner area is outside of the 95% confidence limits for the low-NO_x burner area (-6.0 to -4.1 mils/year).

If it is believed that the corrosion rate of loss decreases with time (most boiler corrosion coupon data support this concept) and a mils/ $\sqrt{year}$ model is used, then the low-NO_x operating period corrosion loss is statistically significantly higher than the baseline operating loss. 6 of the 7 half wall differences produce a higher loss during low-NO_x operations than the corresponding loss during baseline operation. However, separating the nonburner area from the burner area, it is found that the average difference (-3.05 less -2.12 = -0.93) for the nonburner area is not statistically significant while for the burner area the average difference (-5.05 less -2.58 = -2.47) is statistically significant at the 5% probability level (t=2.44). Thus, it is concluded that the low-NO_x operation produces significantly higher corrosion than baseline operation within the burner area.

Figure 3-11 presents a visual comparison of 5 month baseline and 12 month low-NO_x data for average tube wall thickness loss of nonburner area (omitting right wall) and burner area. The projected baseline data on a mils per year basis are shown as dashed lines on Figure 3-11. The 12-month projected nonburner area value of -3.30 mil loss is very close to the actual -3.05 mil loss experienced during the low-NO_x operating period. However, the projected baseline operation, burner area corrosion loss of 4.05 mils is less than the actual low-NO_x operation loss of 5.05 mils. This latter difference is not statistically significant when allowance is made for the uncertainty of both of these loss averages. Note, however, that the 12 month projected baseline operation loss of 2.58 mils for the mil per $\sqrt{year}$ model is statistically significantly less than the 5.05 mils per $\sqrt{year}$ loss during the low-NO_x operation. Thus, the conclusion reached depends upon which model is accepted.

It should be realized that if the mil/$\sqrt{year}$ model is assumed, then the projected loss will be significantly less than if the linear relationship of mils/year is used. Table 3-37 presents projected wall tube thickness loss data (mils) based on a mil/year and a mil/ $\sqrt{year}$ basis for 1, 4 and 16 years. Obviously these projected values are subject to a large, unknown level of uncertainty.

Figure 3-11

COMPARISON OF 5 MONTH BASELINE AND 12 MONTH LOW NO_X CORROSION DATA

BY ULTRASONIC MEASUREMENT

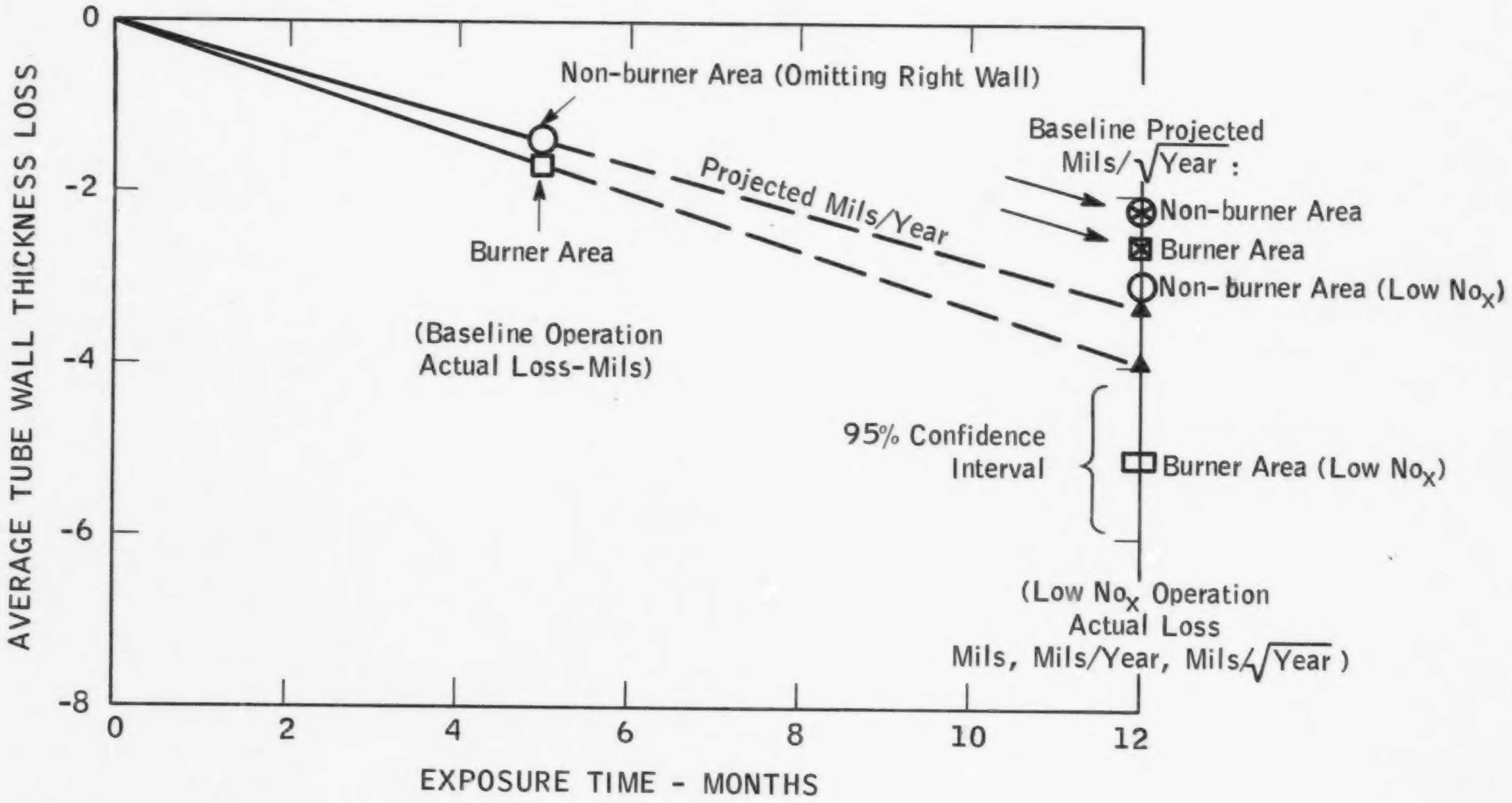


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TABLE 3-37

PROJECTED TUBEWALL THICKNESS LOSSES (MILS)

Furnace Area	Operating Mode	Projection Model					
		Mils per Year			Mils per $\sqrt{\text{Year}}$		
	No. of Years	1	4	16	1	4	16
Nonburner	Baseline	3.3	13.2	52.8	2.1	4.2	8.4
	Low NO_x	3.0	12.0	48.0	3.0	6.0	12.0
Burner	Baseline	4.0	16.0	64.0	2.6	5.2	10.3
	Low NO_x	5.0	20.0	80.0	5.0	10.0	20.0

It is readily apparent from Table 3-37, that the choice between models has a much larger effect on the 4 and 16 year projected figures than the difference between baseline and low NO_x operating results.

3.2.3 Wall Tube Corrosion Test Panels

In Section 2.3.3, the plans and procedures for constructing, installing and measuring the test panels were described. In this section, the measurement data will be presented, statistical analysis will be discussed with the resulting conclusions. The test program was designed to answer the following questions objectively:

(1) Are tubes constructed of ASTM steel specifications SA-210 grade A1 and SA-213 grade T2 equally corrosive when exposed to furnace operation:

  (a) within the burner elevation and
  (b) outside (by at least 20 feet) the burner elevation?

(2) Are corrosion rates of fireside furnace tube walls different at different furnace locations when exposed to: (a) "baseline" operation and (b) staged combustion for "low-NO_x" operation?

(3) Are corrosion rates higher under "low-NO_x" operating conditions than under baseline operating conditions? Does this difference, if any, depend upon furnace location?

Additionally, the influence of the air injection system in the rear hopper slope would be evaluated to the extent possible.

Table 3-38 contains a summary of ultrasonically measured tube wall thickness changes occurring as a result of test exposure as reported by Foster Wheeler Energy Corporation*. Average thickness changes in mils are presented for both hot and cold sides of each of the five initial tubes and the two replacement tubes of each of the eight test panels. Each hot side average change is calculated from 10 to 17 sets of data while the cold side changes are calculated from 8 to 10 sets of data. The exposure times are four months ("low-NO_x" operation between 12/77 and 4/78), 13 months (5 months baseline and 8 months "low-NO_x" operation between 5/76 and 11/77) and 17 months (5 months baseline and 12 months "low-NO_x" operation between 5/76 and 4/78). Tubes numbered 1, 3 and 5 were constructed from ASTM specification SA-210 grade A1 steel and tubes numbered 2 and 4 were made from ASTM specification SA-213 grade T2 steel. Replacement tubes were constructed of SA-210 grade A1 which is the same material used in fabricating the original furnace tubes of Crist No. 7 boiler.

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*The reader should note when comparing Table 3-38 with Table 2 (Appendix H), that the exposure times reported in Table 3-38 have been corrected (by subtracting out boiler down-time) to represent total on-line time, while the times shown in Table 2 represent total elapsed time between measurements, and include boiler outages.

TABLE 3-38

SUMMARY OF ULTRASONICALLY MEASURED TUBE WALL THICKNESS CHANGES OCCURRING AS A RESULT OF TEST EXPOSURE (AVERAGED VALUES, IN MILS)

Panel No.	Side (*)	TUBE NO.						
		1	2	3	4	5	RP-1	RP-2
1	HS	- 4.5	- 1.6	- 1.5	+ .9	- 1.4	+ 1.5	- 1.1
	CS	- 1.5	- .4	- 2.1	+ 1.0	- .9	+ .3	- 1.8
	TM	17	17	17	13	13	4	4
2	HS	+ .47	+ .59	- 2.3	- 2.4	- 1.6	+ 1.2	+ 1.6
	CS	+ .50	+ .63	- 1.1	- 1.5	- 1.2	+ 1.2	- .5
	TM	13	13	17	17	17	4	4
3	HS	-15.3	-12.9	-11.1	-14.6	-13.2	+ 1.1	+ 2.0
	CS	- 1.4	+ .42	- .3	+ .3	- 2.3	+ 1.8	+ .8
	TM	13	13	17	17	17	4	4
4	HS	+ 6.6	-15.8	-20.9	-20.1	-49.9	+ .9	+ 2.0
	CS	+ .4	+ .4	- 1.3	+ 1.4	- .1	+ 3.0	- 1.7
	TM	17	17	17	13	13	4	4
5	HS	- 1.9	- .3	- 3.6	- 2.3	- 3.8	+ 2.0	+ .9
	CS	+ .7	+ .1	- .3	- 1.9	- 1.6	0	+13.4
	TM	13	13	17	17	17	4	4
6	HS	-10.7	- 9.3	- 8.5	- 7.5	- 7.1	+ 2.0	+ 2.8
	CS	--	--	- .5	- 2.1	- 3.0	+ 2.9	+ 2.8
	TM	17	17	17	13	13	4	4
7	HS	- .7	1.8	- 2.1	- .3	- .4	+ 1.8	+ .4
	CS	+ 1.0	.6	- .7	+ 1.7	+ 1.3	+ 2.6	+ 2.8
	TM	17	17	17	13	13	4	4
8	HS	+ .6	0	- 1.2	- .5	+ .4	+ 1.9	+ 1.9
	CS	+ .8	+ 1.9	+ .6	+ 1.8	+ 2.8	+ 1.4	+ .9
	TM	13	13	17	17	17	4	4

(*) HS = Hot Side
CS = Cold Side
TM = Exposure Time in months
Tube Material: ITP 1, 3, 5 - SA210
ITP 2, 4 - SA213T2
RP1 }
RP2 } - SA210

ITP = Initial Test Panel
RP = Replacement Panel

See text (Section 3.2.3) for further explanation of exposure times.

Figure 3-12 is a graph of the average change in tube, hot-side, wall thickness for each of the five initial tubes in each panel. Two tubes from each panel were removed and measured after 13 months exposure, while the other three tubes were exposed for a total of 17 months furnace operation before final measurement. The average change in mils are plotted for each of the 5 tubes of each panel in order from No. 1 through No. 5 with symbols to indicate both types of steel and exposure time. The results for the four panels outside of the burner elevation are plotted first (panels 1, 2, 7, and 8) followed by the panels located within the burner elevation (3, 4, 5 and 6).

Visual examination of Figure 3-12 immediately reveals several interesting points which will be statistically tested for significance:

(1) Panels outside of the burner elevation (panels 1, 2, 7 and 8) showed minor or no change in hot-side tube wall thickness change.

(2) Panels 3, 4, and 6 exposed within the burner elevation showed considerably higher levels of wall-tube thickness loss than the other 5 panels.

(3) The data points representing tubes 1 and 5 from panel 4 were abnormally high (plus and minus respectively).

(4) Both metal types appear to give about equal metal losses within each panel.

Table 3-39 presents the hot side test panel measurements for statistical analysis by metal type. Table 3-39A presents the 13-month exposure data and Table 3-39B presents the 17-month exposure data. The paired difference in average tube hot side wall thickness between metal types SA-210 and SA-213 are shown for each panel. The data for panels located in the non-burner elevation (1, 2, 7 and 8) are separated from the data for panels located within the burner elevation (3, 4, 5, and 6). Paired and unpaired "t" tests for differences between the average corrosion rates of the two types of steel showed no statistically significant differences for the 4 group panels (nonburner and burner elevation panels for 17 month and 13 month exposures). However, it should be noted that each of the four panel group average differences showed a slight advantage of SA-213 type steel over SA 210 type steel (+0.43, +1.47, +0.11 and +1.09). Unfortunately, more data would be required to demonstrate that the apparent advantage of SA-213 is real.

Figure 3-13 is a simplified side elevation of Crist No. 7 boiler showing the location of the 8 corrosion test panels in relationship to the 3 rows of burners in the front and rear furnace walls. Also shown above each of the panels are the average

Figure 3-12

TEST PANEL MEASUREMENTS BY METAL TYPE - 5 TUBES PER PANEL
(AVERAGE CHANGE IN TUBE HOT SIDE WALL THICKNESS - MILS)

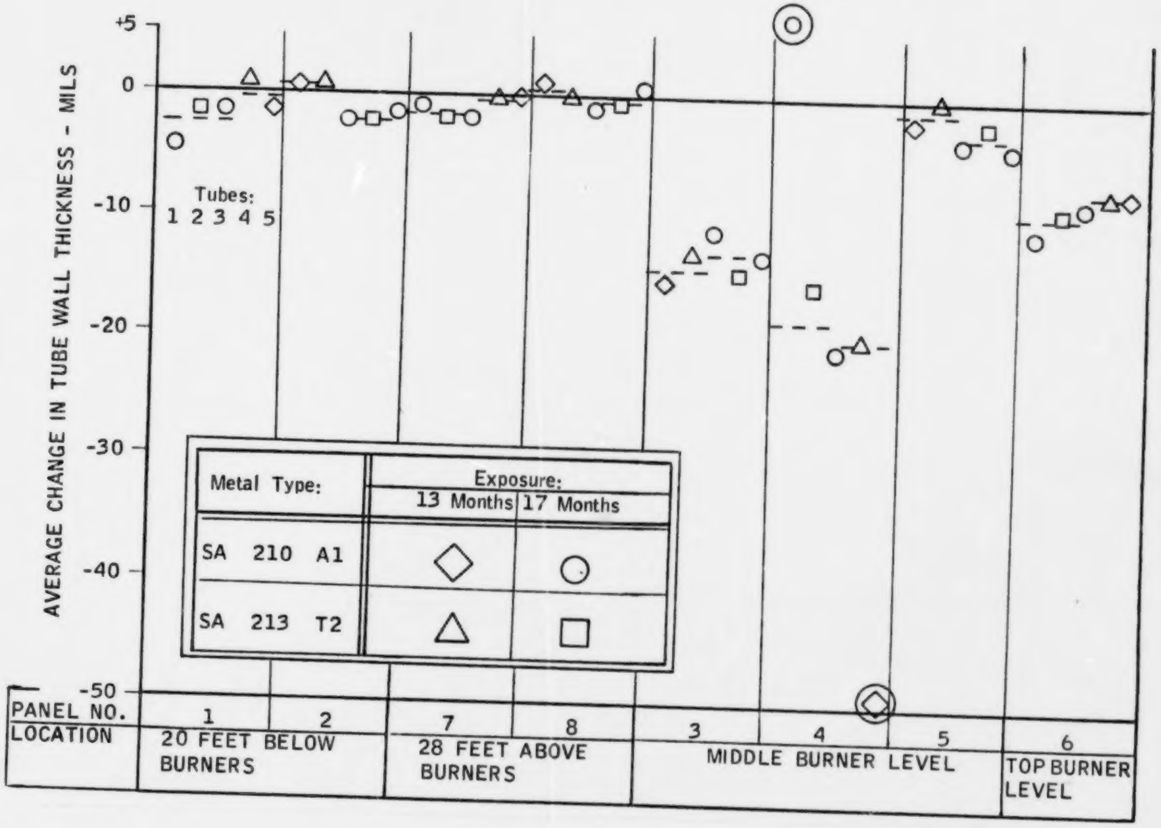


TABLE 3-39

TEST PANEL MEASUREMENTS BY METAL TYPE
(Average Change in Tube Hot Side Wall Thickness - Mils)

A. 13 Month "Mixed" Operation (5/76 to 11/77)

Panel Number		Metal Type: SA-210 A1	Metal Type: SA-213 T2	Difference (Mils)	Panel Average
1	Burner Zone	-1.4	+0.9	+2.3	-0.25
2		+0.47	+0.59	+0.12	+0.53
7		-0.3	-0.4	-0.1	-0.35
8		+0.6	0.0	-0.6	+0.30
	Average	-0.16	+0.27	+0.43	+0.06
3	Non Burner Zone	-15.3	-12.9	+2.4	-14.1
4		-20.1	-49.9*	(-29.8)	(-35.0) -20.1
5		-1.9	-0.3	+1.6	-1.1
6		-7.5	-7.1	+0.4	-7.3
	Average	-11.20	(-17.55)-6.77	(-6.35) + 1.47	(14.38) -10.65

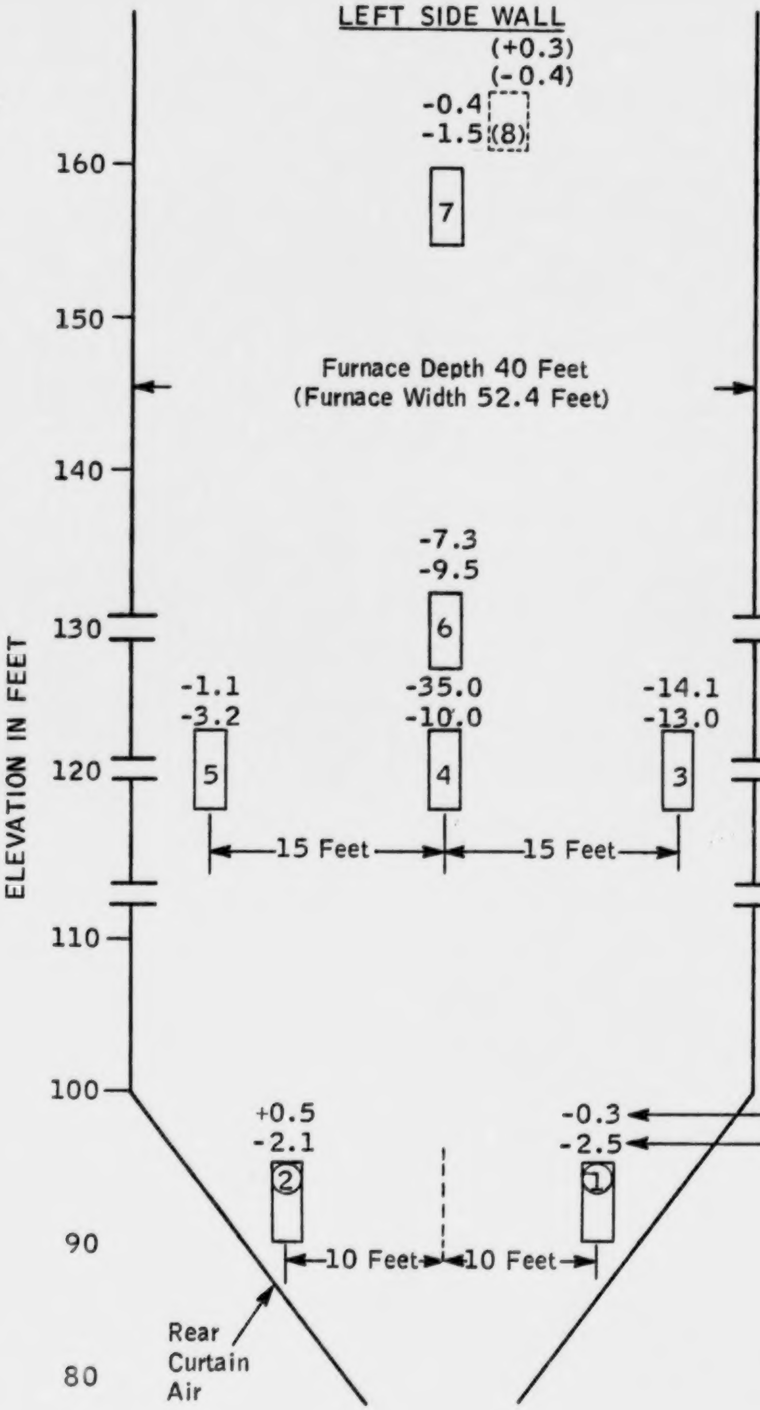
B. 17 Month "Mixed" Operation (5/76 to 4/78)

Panel Number		Metal Type: SA-210 A1			Metal Type: SA-213 T2	Difference (Mils)	Panel Average
		Tube A	Tube B	Average			
1	Burner Zone	-4.5	-1.5	-3.0	-1.6	+1.4	-2.53
2		-2.3	-1.6	-1.95	-2.4	-0.45	-2.10
7		-0.7	-2.1	-1.4	-1.8	-0.4	-1.53
8		-1.2	+0.4	-0.4	-0.5	-1.0	-0.40
	Average	-2.18	-1.20	-1.69	-1.58	+0.11	-1.64
3	Non Burner Zone	-11.1	-13.2	-12.5	-14.6	-2.45	-12.97
4		+ 6.6*	-20.9	(-7.15) -20.9	-15.8	(-8.65) + 5.1	(-10.03) -14.02
5		- 3.6	- 3.8	-3.7	- 2.3	+ 1.4	- 3.23
6		-10.7	- 8.5	-9.6	- 9.3	+ 0.3)	- 9.50
	Average	(-4.7) -8.5	-11.6	(-8.15) -11.59	-10.5	(-2.35)+1.09	(-8.93) - 9.93

*Outlier data.

Figure 3-13

TEST PANEL MEASUREMENTS AND LOCATIONS
(AVERAGE CHANGE IN TUBE WALL THICKNESS - MILS)


LEFT SIDE WALL
(+0.3)
(-0.4)
-0.4
-1.5
(8)
7
160
150
Furnace Depth 40 Feet
(Furnace Width 52.4 Feet)
140
-7.3
-9.5
6
130
-1.1
-3.2
-35.0
-10.0
-14.1
-13.0
120
5
4
3
15 Feet
15 Feet
ELEVATION IN FEET
110
100
+0.5
-2.1
-0.3
-2.5
②
①
90
10 Feet
10 Feet
Rear
Curtain
Air
80
BURNERS:
TOP
MIDDLE
BOTTOM
Exposures:
13 Months
17 Months

Note: Panel No. 8 was located in the right side wall opposite Panel No. 7 in the left side wall.

changes in tube hot side wall thickness for both the 13 month and 17 month mixed (baseline and "low-NO_x") operations. As seen earlier, relatively low corrosion rates were experienced on panels 1, 2, 7 and 8 located at some distance from the burners. Of the panels within the burner zone, panel 5 closest to the rear wall, experienced considerably less corrosion than panels 3, 4 and 6. It should be pointed out that the hopper air injection system was also on the rear wall. And, even though panel No. 5 was far from the injection ports, it was nevertheless, the closest of all the panels to these air ports. The possible influence of air injected at the rear hopper slope on panel No. 5 should not be ruled out.

Table 3-40 presents the corrosion test panel measurements for statistical analysis. Columns D and E present the 13 and 17 month mixed operation data discussed above from Table 3-39. Columns A and B present test panel measurement data for exposure during 5 months baseline operation and 12 months "low-NO_x" operation. Column C presents data (from Table 3-40) for the two replacement tubes which were exposed during the last 4 months of the "low-NO_x" operating period. To facilitate comparisons of different length operating periods, the average change in tube wall thickness is shown in mils per year as well as mils.

The results of statistical analysis of Table 3-40 can be summarized as follows:

(1) The average loss in tube hot side wall thickness during the 5 month baseline operation was about 2 mils (or 5 mils per year) except for panel number 5 which experienced about double that loss. Panels in the non-burner area experienced about the same loss as panels located in the burner area (except panel number 5).

(2) The average loss in tube hot side wall thickness was about 5 mils (or 5 mils per year) during the 12 month "low-NO_x" operating period. However, the test panels located in the burner area experienced a significantly higher loss level (10 mils per year) than the panels located within the non-burner area (+0.2 mils per year).

(3) Comparing the corrosion rates (mils per year) for the 5 month baseline and 12 month "low-NO_x" operating periods revealed:

    (a) panels in the non-burner area experienced significantly less corrosion during the "low-NO_x" operation than during the baseline operation (+0.2 vs -5.3 mils per year) and

    (b) the test panels within the burner elevation experienced significantly greater corrosion during the "low-NO_x" operating period than during the baseline operating period (10.4 vs 6.2 mils/year). No explanation could be found for the result under 3(a).

TABLE 3-40

TEST PANEL MEASUREMENTS
(Average Change in Tube Hot-Side Wall Thickness)

Test Panel Number and Location	Baseline(A) Operation-5 Mo. (5/76 to 10/76)			Low NO_x(B) Operation-12 Mo. (11/76 to 4/78)		"Low NO_x"(C) Operation-4 Mo. (12/77 to 4/78)			"Mixed"(D) Operation-13 Mo. (5/76 to 11/77)			"Mixed"(E) Operation-17 Mo. (5/76 to 4/78)		
	Mils	(n)	Mils/Yr.	Mils/Yr.	(n)	Mils	(n)	Mils/Yr.	Mils	(n)	Mils/Yr.	Mils	(n)	Mils/Yr.
Non-Burner Area (20 Feet Below Burners)														
1. Left Wall-Front	-1.9	(6)	-4.6	-1.2	(4)	+1.3	(20)	+3.9	-0.2	(34)	-0.2	-2.5	(51)	-1.8
2. Left Wall-Rear (28 feet above burners)	-2.4	(8)	-6.0	+0.4	(5)	+1.4	(20)	+4.2	+0.5	(34)	+0.5	-2.1	(51)	-1.5
7. Left Wall-Center	-2.3	(6)	-5.4	+1.3	(5)	+1.1	(18)	+3.3	-0.4	(30)	-0.4	-1.5	(42)	-1.1
8. Right Wall-Center	-		-	-	-	+1.9	(20)	+5.7	+0.3	(34)	+0.3	-0.4	(51)	-0.3
Average	-2.20	(20)	-5.33	+0.17	(14)	+1.42	(78)	+4.26	+0.05	(132)	+0.05	-1.62	(195)	-1.18
Burner Area (Middle Burner Level)														
3. Left Wall-Front	-1.7	(7)	- 4.2	- 8.7	(4)	+1.6	(18)	+4.8	-14.1	(30)	-12.9	-13.0	(42)	-9.2
4. Left Wall-Center	-1.5	(7)	- 3.5	-12.8	(3)	+1.4	(18)	+4.2	-35.0	(30)	-32.3	-10.0	(40)	-7.1
5. Left Wall-Rear (Top Burner Level)	-4.4	(5)	-10.6	-		+1.4	(18)	+4.2	- 1.1	(30)	- 1.0	- 3.2	(42)	-2.3
6. Left Wall-Center	-2.6	(8)	- 6.4	- 9.7	(4)	+2.4	(18)	+7.2	- 7.3	(30)	- 6.7	- 9.5	(45)	-6.7
Burner Area Average	-2.55	(27)	- 6.2	-10.40	(11)	+1.70	(72)	+5.10	-14.4	(120)	-13.3	- 8.92	(169)	-6.30
Grand Average	-2.40	(47)	- 5.72	- 5.12	(25)	+1.56	(150)	+4.68	-7.16	(252)	-6.61	- 5.28	(364)	-3.73

(n) Number of paired measurements used in calculation average tube wall thickness changes.

(A) 5 tubes per panel. Initial measurements in laboratory; final measurement in the field.
(B) 3 tubes per panel. Initial measurements in the field; final measurements in the laboratory.
(C) 2 replacement tubes per panel. Initial measurement in the field; final measurement in the laboratory.
(D) 2 tubes per panel. Initial and final measurements made in the laboratory.
(E) 3 tubes per panel. Initial and final measurements made in the laboratory.

(4) Measurements on the replacement tubes, exposed for the last four months of "low-NO_x" operation, showed no metal loss and the small gain shown must be due to measurement bias or miscalibration.

(5) Columns (D) and (E) of Table 3-40 containing measurement data representing both baseline and "low-NO_x" operation lead to similar conclusions as column (B) "low-NO_x" operation. Table 3-41 has been constructed to make this comparison more meaningful. The 17 month "mixed" operation data has been used to estimate 12 month "low-NO_x" operation measurements by deducting the 5 month baseline operation data measured in the field. The estimated 12 month "low-NO_x" operation data is very similar to the actual field measured 12 month "low-NO_x" operation measurements ($r=0.91$) and statistical analysis using the estimated results lead to the same conclusions as use of the field measurement data.

In summary, the following tentative conclusions can be stated for the analysis of corrosion data from test panels exposed to furnace conditions at Crist No. 7 Unit. These conclusions may or may not be supported by analysis of the ultrasonic wall tube and corrosion probe data.

(1) Furnace tubes constructed of ASTM steel specifications SA-210 grade A1 and SA-213 grade T2 have very similar corrosion rates when exposed to furnace operations;

  (a) within the burner elevation and (b) outside the burner elevation.

(2) When exposed to baseline operation, corrosion rates of tube fireside walls are generally similar at different sidewall furnace locations (below, within and above the burner elevations). The average corrosion rate is about 5 mils per year during the first 5 months of exposure. (95% confidence limits are 3.8 to 6.2 mils/year.)

(3) During "low-NO_x" operation, corrosion rates of tube fireside walls, within the burner elevations are about 10 mils/year while tubes at least 20 feet above or below the burner show little or no corrosion.

3.2.4 Correlation of Test Panel, Furnace Tube and Probe Coupon Corrosion Data

In Sections 3.2.1, 3.2.2 and 3.2.3 corrosion data were presented and discussed for probe coupons, test panels and furnace wall tubes, respectively. In this section, the corrosion results for all three methods will be presented together for discussion and correlation purposes. First, a summary of the statistically significant results obtained from each corrosion measurement

TABLE 3-41

COMPARISON OF FIELD AND LABORATORY MEASUREMENTS (MILS)

Panel No.:	Field Measurements: 5 Month Baseline Operation	Field Measurements: 12 Month "Low NO_x" Operation	Lab Measurements: 17 Month "Mixed" Operation	Lab Measurements: Estimated 12 Month "Low NO_x" Operation*
Outside Burners				
1	-1.9	-1.2	-2.5	-0.6
2	-2.4	+0.4	-2.1	+0.3
7	-2.3	+1.3	-1.5	+0.8
Average	-2.20	+0.17	-2.03	+0.17
Inside Burners				
3	-1.7	-8.7	-13.0	-11.3
4	-1.5	-12.8	-10.0	-8.5
5**	-4.4	–	- 3.2	+1.2
6	-2.6	-9.7	-9.5	-6.9
Average	-2.55	-10.40	-8.92	-8.5

*17 month "mixed" operation minus 5 month baseline operation = estimated 12 month "low NO_x" operation measurements.

**For panel No. 5, field data is not available for the 12 month Low-NO_x period. (The estimated 12 month data, last column on this table, has been used instead.)

method will be presented. These results will be compared and discussed. Finally, a table containing a summary of the left side wall corrosion measurements will be presented for discussion and conclusions.

Analysis of the corrosion probe coupons in Section 3.2.1 led to the following observations:

- The corrosion rate (mils per year) of probe coupons decreases with exposure time through at least 1000 hours.
- During one day tests, probes exposed within the burner level of the furnace sidewalls experienced greater corrosion rates, than probes exposed outside of the burner levels. This was true for both baseline and low-NO_x operation.
- Probes exposed for periods of 240 to 1000 hours experienced no significant differences due to furnace location (burner vs nonburner area) or furnace operating mode (baseline vs low-NO_x operation).

Analysis of the furnace tube, ultrasonic thickness measurement data in Section 3.2.3 led to the following results:

- The minimum standard error or uncertainty of the difference between single pair of before and after exposure measurements is 2.4 mils.
- There was no statistical evidence of biased corrosion measurements caused by sandblasting tubes (for ultrasonic measurement) during the baseline operating period of 5-month duration.
- There was some evidence of slightly increased corrosion (average of 0.5 mil) caused by sandblasting tubes over the entire 17 month exposure period comprising both baseline and low-NO_x operation. However, this possible bias was too small and inconsistent to require adjustment in further statistical analysis.
- The variation among measurement level corrosion averages within half-walls is uniform during both baseline and low-NO_x operation.
- Under baseline operation, Crist No. 7 furnace experienced significant corrosion loss only on the right sidewall. For the entire furnace the average tube wall metal loss was 2.2 mils, with 95% confidence limits of 1.5 to 2.8 mil loss over the 5-month baseline exposure period.

- Under the 12-month, low-NO_x operation, Crist No. 7 furnace experienced a significant level of wall tube metal loss on all half walls except the nonburner areas of the right and rear walls. For the furnace as a whole, the average metal loss on burner area half-walls was 5.05 mils which was significantly higher than the 2.11 mil loss of the nonburner area half walls.

- The average corrosion loss during low-NO_x operation was significantly higher than the average corrosion loss during baseline operation within the burner area assuming a "mils per $\sqrt{\text{year}}$" model (5.05 vs 2.58 mils/$\sqrt{\text{year}}$ loss).

Analysis of the specially constructed wall tube test panels in Section 3.2.2 led to the following results:

- Although SA 213 type steel experienced less corrosion than SA 210 type steel, the difference was not statistically significant.

- During the 5-month baseline operation, the average corrosion loss was about 2 mils (or 5 mils/year) except for panel No. 5 which experienced about double this loss, and panels in the nonburner area experienced about the same loss as panels located within the burner area.

- Table 3-40 shows that during the 12-month low-NO_x operating period, the test panels located within the burner area experienced a significantly higher loss level (10 mils) than the panels located outside the burner area (0 mils). The possible exception is panel No. 5 which could be the result of a calibration error, or effects of curtain air, or an imbalance between front and rear combustion air.

- Comparing the corrosion rates (mils/year) for the 5-month baseline and 12-month low-NO_x operating periods revealed:

  (a) Panels in the nonburner area experienced significantly less corrosion during the low-NO_x than during the baseline operation (+0.2 vs -5.3 mils/year).

  (b) Panels within the burner elevation (with the possible exception of panel No. 5, just discussed) experienced significantly greater corrosion during the low-NO_x operation than during the baseline operation (-10.4 vs -6.2 mils/year). (See Table 3-40.)

Although the different corrosion measurement methods used did not produce identical loss data, there was considerable agreement on relative results as shown in Table 3-42. On the

TABLE 3-42

QUALITATIVE SUMMARY OF CORROSION MEASUREMENTS

Method Used to Obtain Corrosion Measurements		Baseline Operation	Low NO_x Operation	Low NO_x vs Baseline Operation
1. Furnace Wall Tubes (Ultrasonic)		Burner area equal to nonburner area	Burner area loss greater than non-burner area loss	Low NO_x loss > baseline within burner area
2. Test Panel Tubes (Ultrasonic)		No significant differences (except panel No. 5)	Burner area loss greater than non-burner area loss	Low NO_x loss > baseline within burner area. Low NO_x loss < baseline outside burner area
3. Probe Coupons (Weight)	30 Hours Exposure	Burner area loss greater than non-burner area	Burner area loss greater than non burner area loss	
	240-1,000 Hours Exposure	No significant difference between burner and non-burner areas	No significant difference between burner and non-burner areas	No significant difference

average, under low NO_x conditions, corrosion loss as determined by wall measurements, by panels (with the possible exception of panel No. 5) and by probes exposed for 30 hours was greater within the burner area than the nonburner area. Low-NO_x corrosion rates were significantly higher than baseline corrosion rates within the furnace burner area according to both furnace tube and test panel measurements (with the possible exception of panel No. 5); however, low NO_x corrosion rates were significantly lower than baseline corrosion rates on test panels located outside of the burner area.

Table 3-43 presents a summary of Crist No. 7 furnace left side wall corrosion rate measurements for ready comparison purposes. Since seven out of the eight test panels were inserted into the left side wall and there were no test panels or probes inserted into the two burner walls, only data from the left side wall are shown in Table 3-43. Significantly high average corrosion rates are indicated by a single asterisk. Low-NO_x operation corrosion rates that are significantly higher (or lower) than baseline corrosion rates are shown with double asterisks. Examination of Table 3-43 (containing data from Crist No. 7 left side wall only) leads to the same conclusions shown on Table 3-42 for the entire boiler.

Thus, it can be concluded that corrosion rates on Crist No. 7 boiler are about equal within the burner and nonburner areas under baseline operation, while low-NO_x operation produces significantly higher corrosion rates within the burner area than the nonburner area. Corrosion rates decrease with time as shown by probe coupon measurements. Extremely high corrosion rates were not found by any of the three methods for measuring corrosion.

3.3 Relationship Between Furnace Gas Measurements and Corrosion Results

3.3.1 Furnace Gas Tap Results

The purpose of the furnace gas analysis was to try to find locally corrosive environments within the combustion zone. Corrosion rates in these areas could then be studied in greater detail. By comparing baseline gas tap readings with those taken under low-NO_x conditions, one could determine how the corrosion sive potential of the furnace gases was affected by the combustion controls.

Twenty-two of the tests done on Crist No. 7 included furnace gas tap sampling and analysis. Table 3-44 describes the operating conditions and identification numbers for the 22 tests in which furnace gas was sampled.

Each furnace gas tap test was done in conjunction with a flue gas test during which boiler operating parameters were

TABLE 3-43

SUMMARY OF LEFT SIDE WALL CORROSION RATE MEASUREMENTS (MILS/YEAR)

Corrosion Measurement Method	Baseline Operation		Low NO_x Operation		Low NO_x Less Baseline	
	Burner Area	Non-Burner	Burner Area	Non-Burner	Burner Area	Non-Burner
1. Furnace Wall Tubes	1.4	3.2	6.2*	3.9	+3.8**	+0.7
2. Test Panel Tubes	6.2	5.3	10.4*	-0.2	+4.2**	-5.5**
3. Probe Coupons: 500-1,000 Hours***	12.1	11.8	-	11.4	-	-0.4
240-300 Hours	26.9	25.9	20.5	16.4	-6.3	-9.5
24-30 Hours	89.7	82.3	113.6	90.8	+24	+9

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*Burner area average loss significantly higher than nonburner area average at the 5% probability level.

**Low NO_x operation average loss significantly higher or lower than baseline operating corrosion average loss at the 5% probability level.

***In the burner area,corrosion probe tests of more than 500 hours were not performed.

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TABLE 3-44

FURNACE GAS TAP TESTS NUMBERS GROUPED BY TEST CONDITIONS

Load (MW)	Firing Mode	Burner Damper Configuration (Secondary Air Register Settings: Top-Middle-Bottom)*							
		A (33-33-33)		B (40-30-30)		C (55-25-20)		D (60-25-15)	
		Normal Air	Low Air	Normal Air	Low Air	Normal Air	Low Air	Normal Air	Low Air
Near Full (449 - 510)	5			125 126					
	7	59A 61A							
	11				137				
Reduced (350 - 450)	5			200					
	7	56A 57A		132					
	11					91A 93A	94A		96A
	13						89B		
Medium (150 - 350)	1							88A	
	2	55A		130					
	8	53A							
	9							79A	
	13				134 136				
	17	52A							

---

*The values represent the average percent open for the top, middle, and bottom groups, respectively.

recorded in the control room. The test numbers which identified the flue gas tests and control room operating records are the same as the test numbers used to identify furnace gas tap tests with two exceptions:

- When a furnace gas tap test number contained a "letter" suffix, the corresponding flue gas test number is found by simply dropping the suffix. (Example: furnace gas test No. 61A corresponds to flue gas test No. 61.)

- Furnace gas test No. 96A corresponds to duct test No. 95. (This is the only exception to the letter suffix rule just mentioned.)

During furnace gas sampling and analysis, the same gases were monitored as during flue gas tests. However, since the purpose of furnace gas sampling was to find corrosive local environments, only O_2 and CO measurements were examined in detail.

Corrosive reducing environments are identified by low O_2 and high CO concentrations. In such regions, the oxygen is essentially used up, but combustion is still incomplete. That is; the intermediate product, CO, is "looking" for oxygen to complete the conversion of CO to CO_2. Hence the CO is a reducing agent.

Staged combustion means (by definition), that the fuel is burned in stages rather than all at once. Such slow burning is done by with-holding some of the air (required to burn the fuel) until fuel is further downstream in the combustion process.

With staging, the fuel is still traveling through the furnace at the same rate as before, but it is burning more slowly. The result is a longer flame. Hence under staged conditions, one would expect to find un-combusted reactants further along in the stream than without staging. In fact, this does happen.

Figure 3-14 shows the amount of CO in the furnace at a certain point in the combustion process stream. Specifically, that point is elevation No. 1 (see Figure 2-2). It is the uppermost elevation of gas taps and is located 27 feet (8.2 m) above the top-most burner elevation. (The presence of CO signifies incomplete combustion.) Figures 3-15 and 3-16 show the same information, but for points at elevations 2 and 3 which are 8 feet (2.4 m) above, and even with the top burner elevation, respectively (see Figure 2-2).

For elevation No. 2, the reader will notice (Figure 3-15) that as the degree of staging is increased (i.e., as firing pattern goes from mode 5 to mode 13), the amount of CO at this point in the process stream, becomes greater. This indicates that with staging, combustion requires more distance in the process stream to reach completion. In other words, the flame becomes longer (and cooler).

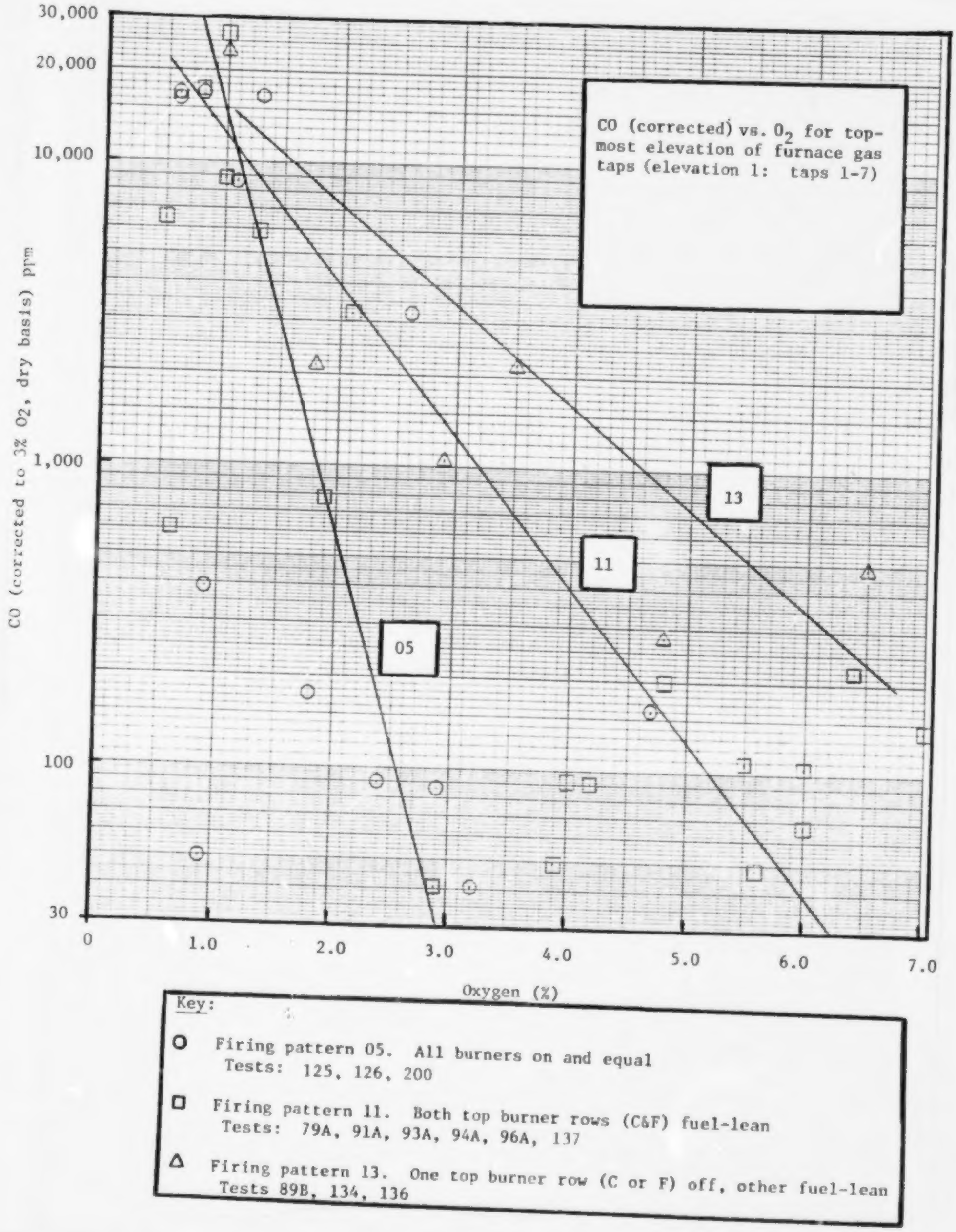

Figure 3-14. CO vs. O$_2$ (for gas taps 1-7).

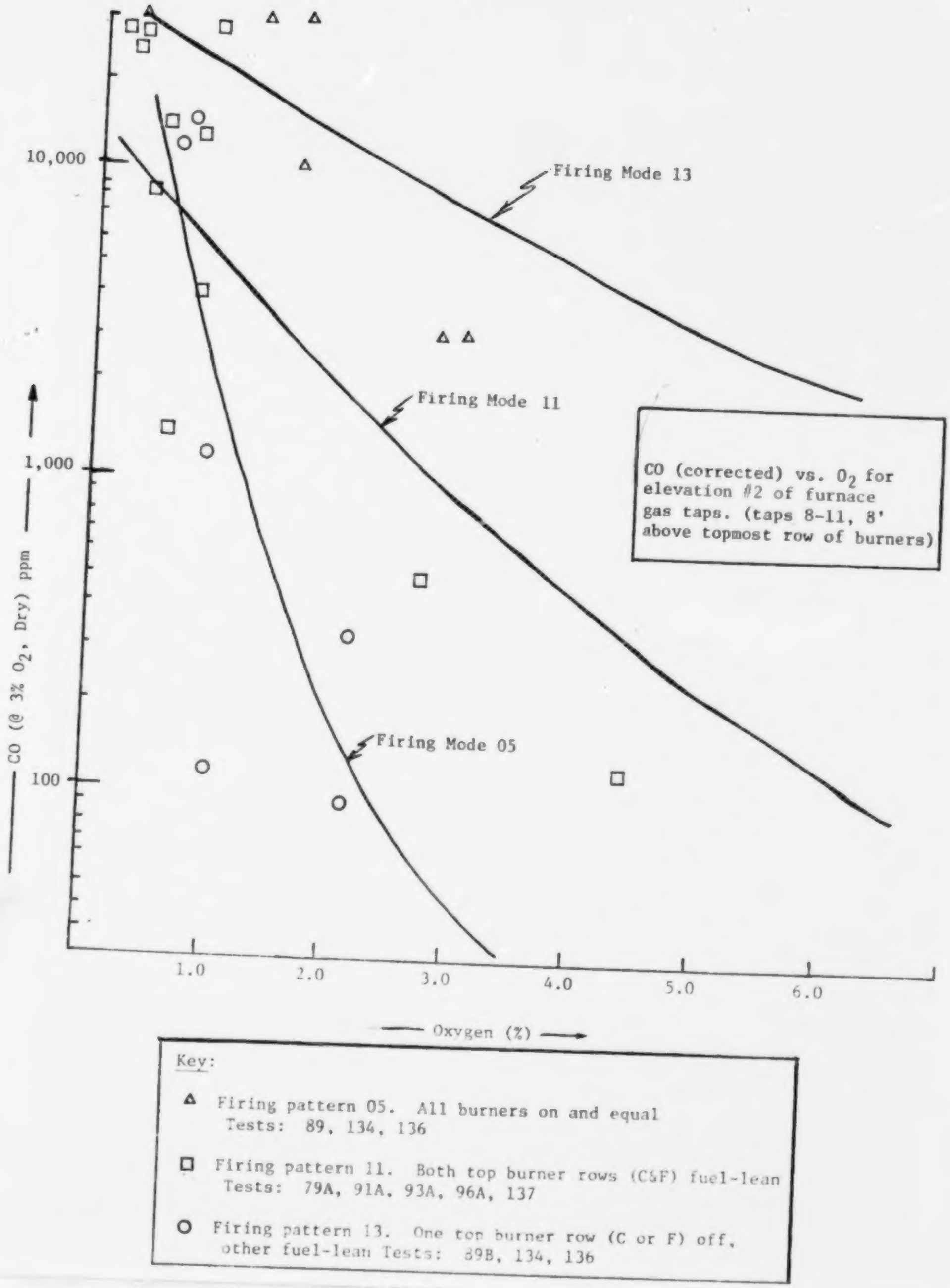

Figure 3-15. CO vs. O_2 (for gas taps 8-11).

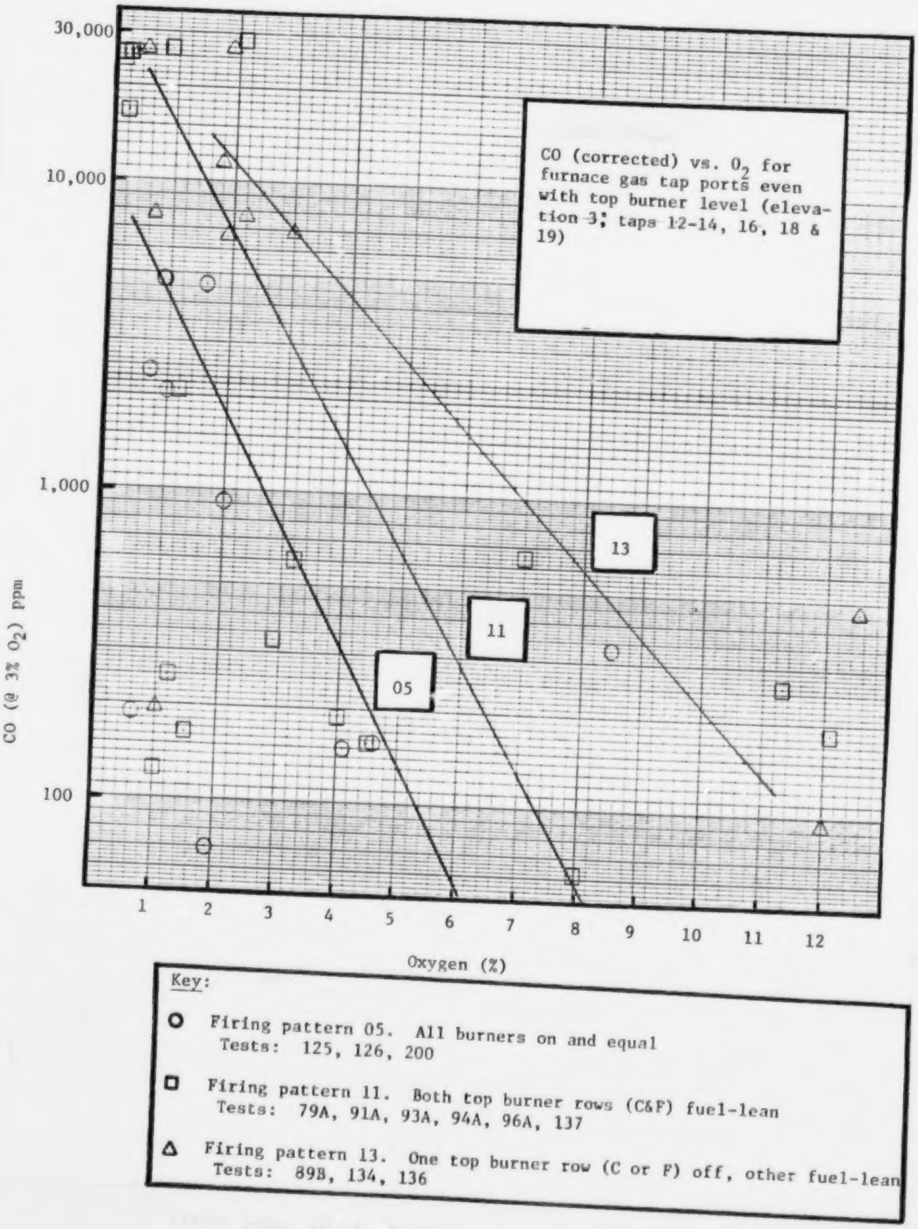

Figure 3-16. CO vs. O_2 (for gas taps 12-14, 16, 18, and 19)

Other samples taken farther downstream indicate that for the degree of staging tested, combustion is always essentially complete by the time the flue gases leave the boiler regardless of the degree of staging used. However, it should be noted that only slight substoichiometric firing was attempted. FWEC has calculated that during these tests, burners were generally operated at about 95-100% of theoretical air flow, even during the best low NO_x conditions tested. The effect of severe staging (burner stoichiometries less than 90%) on CO and unburned carbon was not determined. In fact, to be sure of complete combustion, the staging controls were set up while monitoring flue gas CO concentration. This assured that the combination of staging and low excess air would not lower the total combustion efficiency. In all cases, staged or not, Figures 3-14, 3-15, and 3-16 show that on the average, as oxygen concentration in the furnace decrease, CO levels increase.

During the low-NO_x period of operation, both staging and low total excess air were used to reduce NO_x emission rates. A decrease in total air leads to a more corrosive environment (more CO) above the combustion zone because of the chemically reducing property of the gas. Hence one would expect increased corrosion in this region of the boiler under low-NO_x conditions.

3.3.2 Wall Tube Corrosion Measurements

Table 3-45 lists the actual corrosion rates. Clearly, a higher overall corrosion rate was found in the upper burner region (elevations 3 and 4) during the low-NO_x period than was found here during the baseline period.

When a model assuming decreasing corrosion rate with time (i.e., "$1/\sqrt{\text{year}}$" model) is used, the corrosion rates measured outside the burner zone, become statistically insignificant. However, using the same model, the corrosion rates measured within the burner elevations are meaningful. That is, for the corrosion rate measurements done within the top two burner elevations, (levels 3 and 4) it is statistically significant that a higher corrosion rate was found during the low-NO_x period than was found during the baseline period.

3.3.3 Correlation Between Furnace Gas and Wall Thickness Measurements

Since furnace gas tap results for the top burner elevation have already been discussed, the following discussion will attempt to find a correlation between gas tap measurements and corrosion rates, at the top burner elevation. (This is one of the elevations where corrosion data is statistically significant.)

TABLE 3-45

CORROSION RATES (MILS/YR) AS MEASURED ULTRASONICALLY ON THE LEFT WALL

Elevation (see Figure 2-1)	Baseline	Low NO_x	
1 (27 ft above burners)	7.5	1.9	
2 (8 ft above burners)	5.7	3.0	
3 (at top burner elevation)	3.2	5.5	Burner Zone
4 (at middle burner elevation)	2.1	4.9	
5 (at bottom burner elevation)	6.7	4.4	
6 (13 ft below burners)	5.7	0.5	

Data is from Table 3-28.

For each of the top three elevations of gas taps, significant differences in furnace gas composition are seen (Figures 3-14, 3-15, and 3-16) between baseline (firing mode 05 with high O_2) and low-NO_x (firing modes 11 and 13 with low O_2) conditions. The gas tap data, thus helps predict the increased corrosion rate seen under low-NO_x operation.

But among the top three levels (1, 2, and 3), it has already been stated that the corrosion data was statistically significant only at level 3 (see Figure 2-2). The following discussion deals with how the analysis of the furnace gas sampled here, differs from that of samples taken higher in the boiler.

In this region, (level 3, see Figure 2-2) CO levels (corrected) at low-NO_x conditions were only slightly higher than those in the upper two levels. However in this region (level 3), low-NO_x operation caused oxygen readings to be significantly lower than those at baseline. This was not the case at levels 1 and 2.

The uncorrected CO concentration is considered to be responsible for the corrosive nature of the gas. Upon reexamination of the data, it was found that elevation No. 3 (which had statistically significant corrosion data), was the same elevation that had the high values (uncorrected) of CO concentration, (although the correlation is weak).

The furnace gas tap data used in this analysis is presented in Table 3-46. The location of the gas taps is shown in Figure 2-2. Some averages of CO data (uncorrected) are shown in Table 3-47.

A plot of corrosion rate vs CO concentration in the furnace nace for elevation No. 3, (the one with statistically significant corrosion data) is shown in Figure 3-17. The data is from Table 3-46.

Of course one should not weigh the importance of this plot too heavily since it only contains two data points. Furthermore, other firing modes besides No.11 and No. 13 were used during the low-NO_x period of operation, just as firing mode No. 05 was not used exclusively during the baseline period. Finally, no attempt was made to factor out the effects of damper setting or total air flow. In fact, because of the low air flows used during some of the tests of firing mode No. 05, some of the firing mode No. 05 data may have belonged in the low-NO_x category rather than in the baseline category.

TABLE 3-46

Furnace Gas Tap Data

Test No.	200	52A	53A	55A	56A	57A	59A
Date	6/11/76	11/5/76	11/12/76	11/16/76	12/2/76	12/7/76	12/13/76
Load (MW)	High (450)	Low (260)	Med (310)	Low (162)	High (405)	High (440)	High (470)
Air Dampers*	All 80%	80-40-40	80-40-40	80-40-40	80-40-40	80-40-40	80-40-40
Air Flow	Normal	Normal	Normal	High	Normal	Normal	Normal
Fuel Feeds	All on	A,D,F, off	D & F off	D & E off	D off	D Off	D off

Boiler Exhaust Gas Analysis**

O_2	3.0	7.6	5.6	9.0	4.3	4.3	3.
CO	20	16	18	57	44	11	59
NO_x	558	378	464	687	773	689	745

Furnace Gas Analysis**

	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO
Tap No. 1	4.7	160												
2	1.3	17K	9.0	39					0.6	5200			0.4	26K
3	1.1	8600												
4	0.6	17K	6.0	43					5.1	103			4.0	164
5	0.6	16K												
6	2.6	3200	5.9	26					8.9	120			6.6	126
7	0.7	17K							0.6	2500			1.4	1620
8	1.0	131	9.3	66	1.5	13K	6.5	--	1.9	1300	0.5	9300	0.4	26K
9	0.6	17K	8.0	111	8.5	107	6.0	--	0.5	13K	0.3	13K	0.4	26K
10	0.4	19K			0.3	25K								
11	0.7	13K					6.0	—	1.2	1100	2.9	27K	5.9	494
12	4.6	159			5.5	2500	7.0	—	1.5	2600	0.3	21K	0.4	26K
13	0.9	4800	6.0	243	1.9	15K	6.0	--	4.0	—	0.7	11K	1.4	18K
14	0.7	24K			1.9	1400	10.0	—	6.4	260	7.4	140	5.5	113
18														
19									6.1	1270	1.8	980	4.5	838
20	1.2	2950			0.1	23K			4.4	15K				
21	0.6	24K												
22	0.8	20K			0.1	26K	14.5	--	0.7	2000	0.2	7000	0.4	26K
23	0.7	24K			0.2	19K	12.0	--	6.0	3400	4.9	141	1.8	3800

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* Secondary air register settings (Top-Middle-Bottom)

** CO and NO_x corrected to 3% O_2.
"K" means "multiply by 1,000".

(Continued on next page)

TABLE 3-46
(CONTINUED)

Furnace Gas Tap Data

Test No.	61A	79A	88	89	91	93	94	96
Date	12/14/76	1/13/77	1/27/77	1/28/77	1/31/77	2/1/77	2/1/77	2/2/77
Load (MW)	High (460)	Low (330)	Low (275)	(435)	(440)	(440)	(440)	(450)
Air Dampers*	80-40-40	80-40-40	80-40-40	80-40-40	80-40-40	80-40-40	80-40-40	80-40-40
Air Flow	Low	High	High	Low	High	Normal	Low	Low
Fuel Feeds	D off	C & F low	B & E off	F off	C & F low	C & F low	C & F low	C & F low

Boiler Exhaust Gas Analysis**

O_2	3.1	7.3	5.7	3.5	4.2	4.3	3.2	3.1
CO	57	270	16	198	17	15	17	79
NO_x	712	853	756	529	852	812	816	758

Furnace Gas Analysis**

	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO
Tap No. 1																
2	1.1	14K	5.5	108	2.9	185					4.2	91	3.9	41		
3															6.0	104
4	6.0	64	6.4	219	4.2	24					0.9	777	0.6	6150	5.6	48
5																
6	5.6	125	7.0	136	8.4	164					3.9	49	4.0	92	4.8	197
7	1.2	4700	6.0	67	2.0	169					2.1	3190	1.3	5440	0.5	6500
8	0.9	27K	0.9	3640	7.0	95	0.4	26K	0.7	1560	0.1	26K	0.1	>26K	0.3	2120
9	1.0	27K	2.9	359					4.6	123	0.2	>26K	0.1	>26K	8.2?	122
10													0.1	>26K	0.1	25K
11	2.2	2200	5.0	83	4.2	150	0.3	26K	0.3	7850	0.2	>26K				
12	1.1	27K	1.2	248	2.8	50	0.3	26K			0.1	35K	0.1	>26K	0.1	25K
13	1.4	18K	3.2	599	2.8	523	1.8	11K			0.2	17K	0.1	>26K	4.0	188
14	6.5	120	2.9	328	5.8	102	0.6	7750			1.2	2085	0.2	>26K	4.5	153
18	8.9	150	12.5	184	3.4	129	1.0	197			1.5	164	1.0	124	7.1	100
19	2.3	3060	8.0	62	0.1	13K	0.3	26K	0.2	>26K	0.2	>26K	0.1	>26K	0.1	>26K
20			4.4	1900	3.0	51	0.2	>29K			0.6	26K	0.7	27K	0.5	24K
21																
22			7.1	330	3.0	80	0.2	>29K								
23	2.8	3100	13.1	145	3.0	68	0.4	26K			0.9	2840	2.8	357	4.0	84

---

* Secondary air register settings (Top-Middle-Bottom).

** { CO and NO_x corrected to 3% O_2.
"K" means "multiply by 1,000".

(Continued on next page)

TABLE 3-46
(CONTINUED)

Furnace Gas Tap Data

Test No.	125	126	130	132	134	136	137
Date	2/2/78	2/3/78	2/9/78	2/16/78	2/22/78	3/1/78	3/2/78
Load (MW)	Full (485)	Full (485)	Low (325)	Low (300)	Low (300)	Med (350)	High (485)
Air Dampers*	60-40-40	60-40-40	60-40-40	60-40-40	60-40-40	60-40-40	60-40-40
Air Flow	Normal	Normal	Normal	Normal	Low	Low	Low
Fuel Feeds	All on	All on	A & B off	A off	C off, F low	C off, F low	C & F low

Boiler Exit Gas Analysis**

O_2	4.04	3.15	4.87	5.12	2.48	3.74	2.71
CO	8.8	51.32	13.03	11.13	183	24.0	16.06
NO_x	946	944	760	654	395	520	832

Gas Tap Analyses**

Gas Tap Nos.	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO	O_2	CO
1	2.9	86	0.9	50	4.0	48	6.4	30	1.0	23K	1.8	2151	0.8	17K
3	3.2	41	2.4	90	3.7	49	4.1	26	6.5	487	3.5	2177	1.0	8801
4	1.8	174	0.9	390	5.1	46	4.0	30	4.8	282	2.9	1043	1.0	26K
8	2.2	252	0.5	14K	1.5	434	7.5	103	1.5	28K	2.4	29K	1.2	27K
9	1.3	14K	0.8	3623	5.2	68	6.0	47	1.7	28K	2.8	30K	0.5	16K
10	1.8	93	0.9	1580	5.7	93	4.5	95	2.9	3156	3.2	3210	0.7	24K
12	2.0	9022	0.6	19K	5.0	349	2.0	133	1.9	28K	11.0	49K	16.5	13K
14	1.6	4626	1.1	2000	5.5	78	3.2	164	2.2	7732	3.0	6974	2.1	29K
16	1.9	70	8.5	328	11.1	133	10.6	658	12.0	95	12.5	464	11.3	260
19	4.1	149			9.0	42	7.5	52	1.9	28K	1.2	6340	7.0	649
20	4.0	42	3.4	198	12.0	150	7.2	12	2.2	29K	1.8	643	1.3	5437
23	1.4	24K	0.7	9379	9.5	216	1.3	11	7.4	38K	1.5	2930	1.2	27K
25	1.5	488			15.3	385	10.0	110	8.0	303	4.8	558	0.9	27K

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* Secondary air register settings (Top-Middle-Bottom).

** CO and NO_x Corrected to 3% O_2.
"K" means "multiply by 1,000.

TABLE 3-47

SELECTED FURNACE GAS CO AVERAGES

	Baseline	Low NO_x		
Elevation (see Figure 2-2)	Firing Mode 05	Firing Mode 11	Firing Mode 13	Average of Low NO_x Firing Modes
Top 1	6749	4072	4644	4358
2	9303	12948	18667	15807
3	6556	10115	12378	11246

Values shown represent the average of all furnace gas samples at the indicated elevation for all tests.

Note:

Data is as measured, (dry,) and is not corrected to 3% O_2.

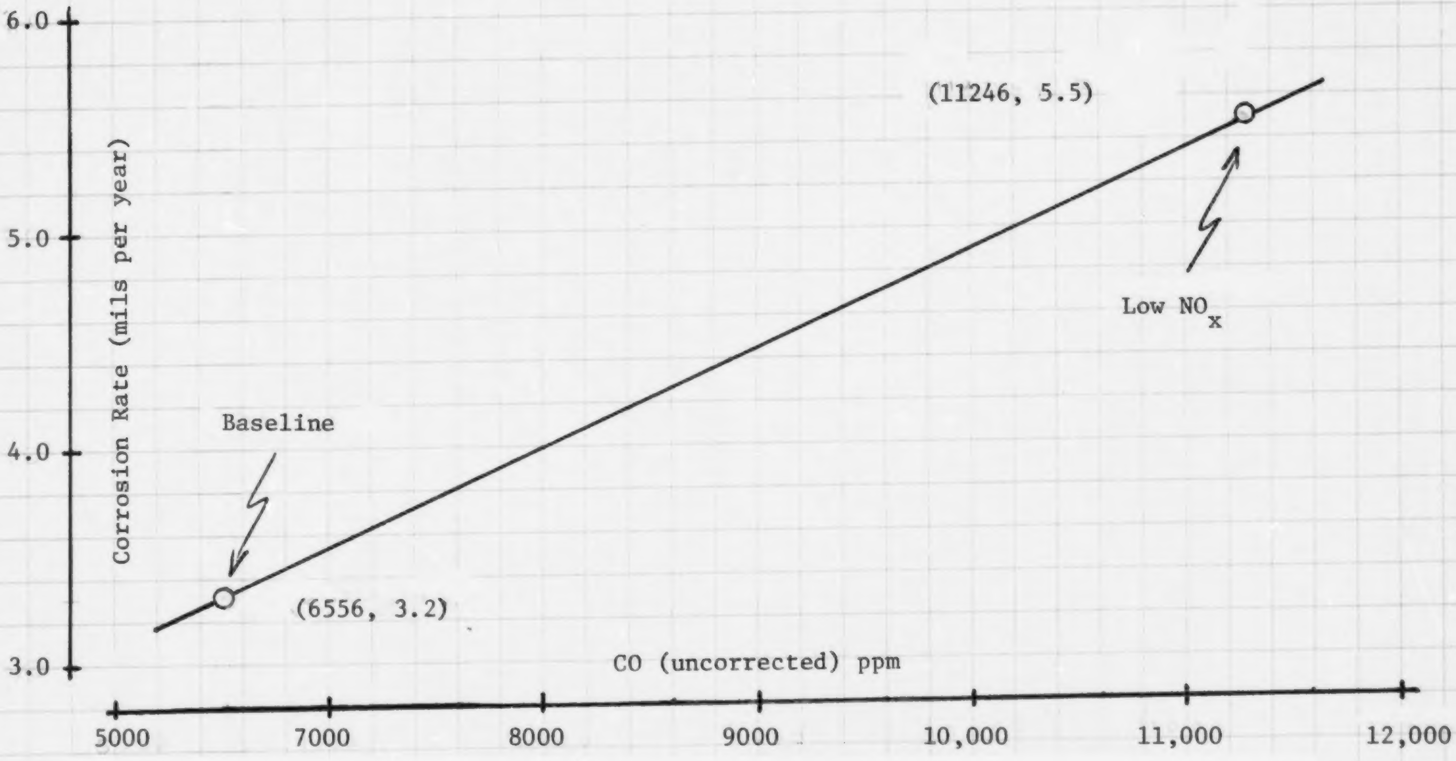

FIGURE 3-17. CORROSION RATE (BY ULTRASONIC MEASUREMENT) VS. CO IN THE FURNACE FOR THE TOP BURNER ELEVATION

CO data is from Tables 3-46 and 3-47.
Corrosion data is from Table 3-28.

Conservatively, one can say that the plot shows that at the top burner elevation, both the corrosion rate and the CO concentration along the furnace wall increase as the boiler's firing mode is changed from baseline to low-NO_x conditions.

3.4 Particulate Emission Results (Precipitator Inlet)

Flue gas particulate data obtained in tests on the No. 7 boiler at Gulf Power Company's Crist Station using EPA approved Method 5 sampling trains are summarized in Table 3-48. Comparing mass loading test results for baseline operating conditions with data obtained under "low NO_x" optimized firing conditions, it can be seen that mass load emissions are only slightly higher during "low-NO_x" operation. This is in line with results from previous tests (7,8) especially in wall fired boilers. The magnitude of the differences in mass emissions is not significant and the collection efficiency required in the electrostatic precipitator to meet the old NSPS standard of 0.1 lb of particulate per million Btu input remains essentially the same as for baseline operation. It may also be noted that the unburned combustible loss (% carbon on particulate) for low-NO_x test No. 153 is 1.71%, or about twice the 0.87% measured in baseline NO_x test No. 152. These differences are comparable to results in prior studies and are undoubtedly reflected in the mass emissions. Also, it would be assumed that these changes would have a corresponding deleterious effect on boiler efficiency. However, as discussed later it will be seen that boiler performance is little affected, being compensated by other operating benefits.

Particle size distribution measurements obtained in the Crist No. 7 test program are summarized in Table 3-49. The data include all of the material collected in the probe and the cyclone for the size range greater than 2.5 micrometers. Comparing the data in the table, it may be seen that there are no significant differences in particle size distribution between low-NO_x and baseline operation in these tests. These data parallel and are very similar to the particle size distribution data developed in previous tests (7). Since no significant differences in particle size distribution measurements occurred between data developed under baseline vs "low-NO_x" firing conditions, especially in the smaller size fractions, the conclusion reached, at least for these tests, is that combustion modifications for NO_x emission control should not materially affect electrostatic precipitator or mechanical collector performance. More data would obviously be helpful, however, to further support this conclusion.

The sampling arrangement used for obtaining particulate particle size distribution information employed the cyclone of the EPA train as the first cut point ahead of the Brink impactor. It is generally accepted that this device collects all material greater than 7 μm in diameter. The fractionation size (D_{50}) for each of the Brink impactor stages is the particle size (aerodynamic diameter in μm) collected with 50% efficiency by the impactor stage. For the Brink impactor the

TABLE 3-48

PARTICULATE EMISSION TEST RESULTS
(INLET TO PRECIPITATOR)

PULVERIZED COAL FIRING

Utility	Date	Test No.	Firing Condition	Load, MW	Emissions				Req. Eff. To Meet 0.1 Lb/10^6 Btu	% Carbon On Particulate	Coal Ash Wt. %	HHV. Wet Btu/Lb
					mg/m^3	GR/SCF	ng/J	Lb/10^6 Btu				
Gulf Power Company, Crist Station Boiler No. 7	6/20/78	150	Base	436	0.686	3.00	2301	5.35	98.1	-	-	-
	6/21/78	151	Low No_x	432	0.874	3.82	1926	4.48	97.8	2.98	12.45	11,263
	6/22/78	152	Base	417	0.864	3.78	2881	6.70	98.5	0.87	16.48	10,782
	6/23/78	153	Low No_x	434	0.909	3.97	2468	5.74	98.3	1.71	14.32	11,033

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TABLE 3-49

PARTICLE SIZE DISTRIBUTION, WT%

GULF POWER COMPANY
CRIST STATION - BOILER NO. 7
PULVERIZED COAL FIRING

Size Range	Baseline Firing			LOW NO_x Firing		
	Test No. 150	Test No. 152	Average	Test No. 151	Test No. 153	Average
>2.5 μm	93.10	94.00	93.6	92.50	89.80	91.2
2.5 μm	2.15	3.48	2.8	3.15	3.68	3.4
1.5 μm	0.90	0.72	0.8	1.12	1.94	1.5
1.0 μm	0.83	0.84	0.7	0.83	1.43	2.3
0.5 μm	1.24	1.20	1.2	1.16	1.84	1.5
<0.5 μm	1.80	0.72	1.3	1.24	1.33	1.3

aerodynamic diameter (D_{50}) for each stage is as noted in Table 3-49 when operated at the prescribed flow rates.

Figure 3-18 presents particle size distribution data vs aerodynamic diameter as a function of solids loading in cumulative percent below the stated size for Gulf Power Company's Crist Station No. 7 boiler.

Referring to the curves shown in Figure 3-18, the data plotted for baseline and "low-NO_x" operation exhibit relatively consistent trends with no indication of adverse side effects attributable to "low-NO_x" combustion modifications. Although some scatter of data is indicated in the smaller size fractions, the range of these variations is not great and the results appear to be within the limits of this type of testing. These data are also consistent with and compare favorably to particle size distribution data developed in prior studies (8).

3.5 Boiler Efficiency Results

Prior studies investigating the effects of low-NO_x combustion modifications on boiler efficiency (7,8) indicated that no significant decreases in boiler efficiency occurred as a result of "low-NO_x" operation; in fact, in some cases small increases were calculated. In tests on Gulf Power Company's No. 7 boiler at the Crist Station potential adverse side effects of low-NO_x operation on boiler efficiency were investigated. The calculation results for the major tests are presented in Table 3-50 along with other pertinent boiler operating information.

Comparing the results tabulated in Table 3-50, it may be seen that the increased carbon content of the particulates resulting from "low-NO_x" firing is not reflected in corresponding decreases in boiler efficiency. Furthermore, there are no major changes in boiler efficiency that reflect major adverse effects due to combustion modifications for low-NO_x operation. The minor differences in boiler efficiency exhibited between baseline and low-NO_x operation may be due to changes in excess air during the tests, and by other factors affecting efficiency, as mentioned above. The overall conclusion from these data is that combustion modifications for control of NO_x emissions, at the levels practiced in these investigations, apparently produced no significant adverse effects on boiler efficiency.

3.6 SO_2/SO_3 Gaseous Sampling Results

Table 3-51 tabulates the results of wet chemistry analysis of flue gas samples extracted from the Crist No. 7 boiler. A comparison of measured SO_x values with calculated values based on 100 percent conversion of fuel sulfur to SO_x is shown for some tests. As discussed in Section 2.7, limited sulfur balance data on coal fired boilers indicates that up to 25% of the sulfur in the coal may be lost within the boiler and fail to show up in the flue gas stream. Referring to Table 3-51, it may be seen that analyzed SO_x values compared to calculated emissions are reasonably in accord with expectations.

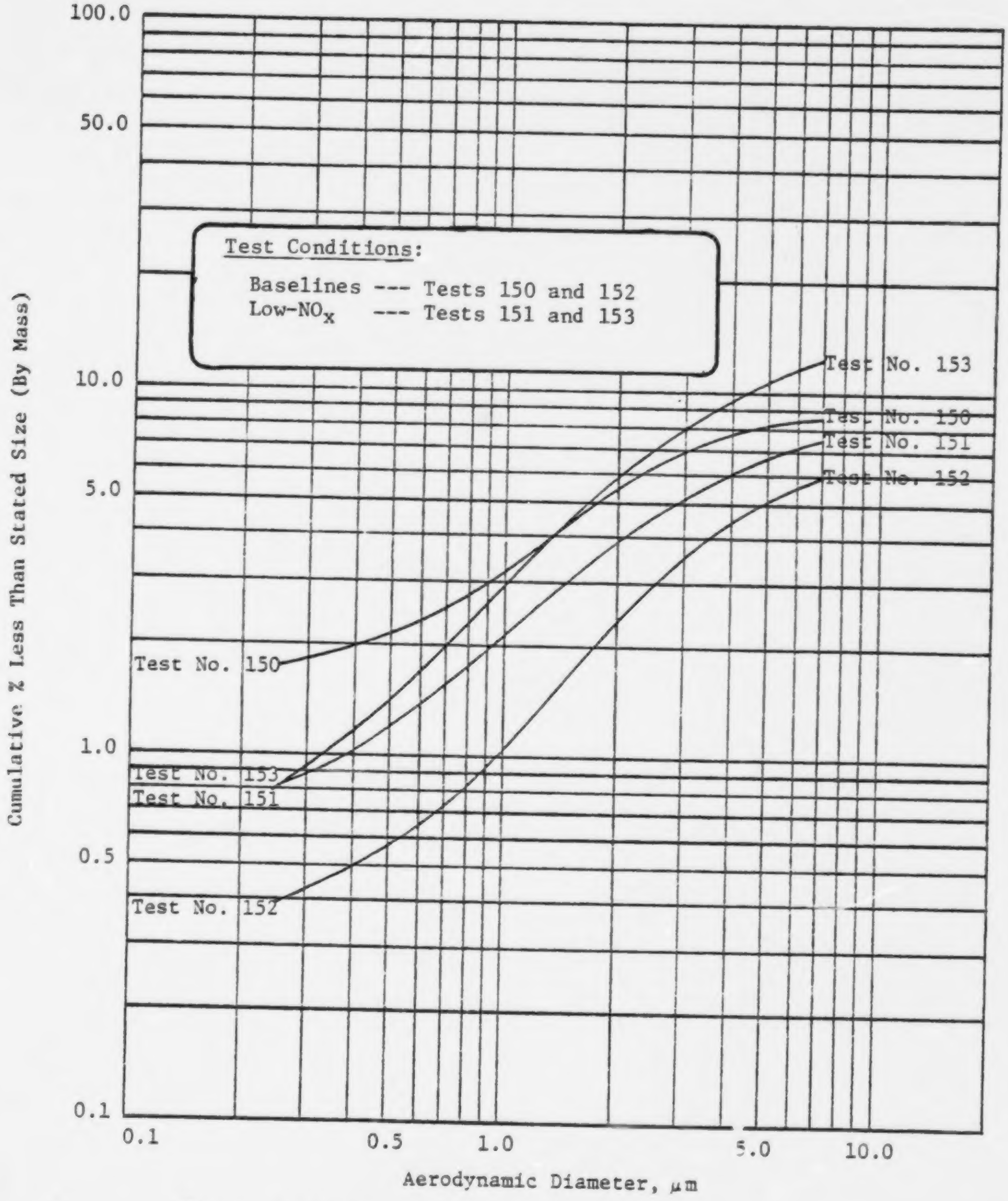

Figure 3-18. Particulate Size Distribution.

TABLE 3-50

SUMMARY OF BOILER PERFORMANCE CALCULATIONS

Boiler Identification	Firing Mode	Test No.	Load, MW	% O_2	NO_x Emmissions, (3% O_2)			Coal Ash, % (Wet Basis)	% Carbon on Particulate	Boiler Efficiency, %
					PPM	Lb/10^6 Btu	ng/J			
Gulf Power Company, Crist Generating Station, Boiler No. 7	Low NO_x	151	432	3.1	508	0.68	291	12.45	2.98	88.92
	Baseline	152	417	5.5	848	1.13	486	16.48	0.87	88.86
	Low NO_x	153	430	1.9	456	0.61	261	14.32	1.71	89.27

TABLE 3-51

GULF POWER COMPANY

CRIST STATION, BOILER NO. 7

WET CHEMISTRY SO_2/SO_3 ANALYSES

PULVERIZED COAL FIRING

Date	Test No.	Firing Condition	Load MW	O_2, %	Calculated SO_x/PPM	Wet Chemistry Analyses				SO_3/SO_2 Ratio, %
						SO_2		SO_3		
						ng/J	PPM	ng/J	PPM	
2/8/76	1F	Baseline	205	9.0	-	1052	1319	27	27	2.1
2/8/76	1G	Baseline	200	9.4	-	1136	1424	12	12	0.8
3/10/76	102	Baseline	400	5.3	-	2108	2643	38	38	1.4
3/11/76	101	Baseline	399	6.1	-	1603	2010	32	32	1.6
12/14/76	60	Baseline	470	4.4	2535	1191	1493	18	18	1.2
2/2/77	97	Low NO_x	450	3.0	-	2302	2887	27	27	.9
2/15/78	131	Low NO_x	300	5.7	2306	2008	2518	31	31	1.2
2/16/78	132	Low NO_x	298	5.1	2683	1909	2394	30	30	1.3
2/22/78	134	Low NO_x	290	2.5	2838	1629	2043	-	-	-
3/2/78	137	Low NO_x	484	2.7	2707	2132	2673	77	77	2.9

Sulfur trioxide analyses for these tests ranged from 12 to 77 ppm well within the range of expected values. Referring to Table 3-51, it may be noted that no significant differences are apparent in SO_x determinations between test results taken at baseline vs low-NO_x firing conditions as might be expected in some installations where the availability of oxygen is limited for the conversion of SO_2 to SO_3 by low excess air firing. Also, as indicated in Table 3-51, SO_3 values are within the anticipated range of 5 percent of total SO_x in the flue gases, affirming confidence in the data.

3.7 SASS Tests - Results and Discussion (17)

The main emphasis of the SASS stack emission tests at the Crist Station was to investigate the extent of potentially toxic emissions from this pulverized coal-fired boiler and, more precisely, to determine whether these emissions are adversely affected by low-NO_x firing conditions. Test 3 run under normal operating conditions established baseline emissions and test 4, conducted at the same load with the boiler operating at the optimum low-NO_x emission firing mode, provided data for the desired comparison. SASS tests 3 and 4 correspond with flue gas tests 152 and 153, respectively.

The following specific difficulties were noted with Level 1 methodologies pertaining to the SASS samples:

- Phthalate contamination (perhaps from plastic sample containers) was identified in infrared analysis and verified by mass spectrometry analysis.
- Poor correlation existed between crude organic quantitation prior to and after liquid chromatographic separation.
- It was necessary for extensive clean-up of the XAD-2 resin prior to the test.
- The use of salt plates for IR resulted in loss of volatile compounds.
- There was not enough flyash particulate for all required tests.
- There was not enough material for mass spectrometry analysis.

Many of these problems have been addressed in the "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)"; EPA-600/7-78-201, NTIS No. PB 293795, October 1978.

Appendix E delineates amendments to the Level 1 methodology.

3.7.1 Metals in Coal

Samples of the coal fired during tests 3 and 4 (baseline and low-NO_x) were analyzed for elemental metals via inductively coupled plasma emission spectroscopy (ICPES). Results are tabulated in Table 3-52. For quality assurance, the table includes analysis results for coal sample no. 1632 from two independent laboratories. One analysis is by the National Bureau of Standards (NBS). The other is Exxon's ICPES analysis of the same sample. It may be seen that relatively good agreement was obtained between the Exxon and the NBS analyses. This gives confidence to the metal data reported for the coal samples in tests 3 and 4.

Referring to Table 3-52, it may be noted that the metals content of the coal fired in tests 3 and 4 is quite uniform. This is not unexpected since the tests were conducted on successive days and the coal quality fed to the boiler normally does not change drastically from day to day even though the supply is from several mines. Other metal concentrations are shown in Table 3-53. (Metal concentrations in the flue gas are presented on Tables 3-62 through 3-64.)

3.7.2 Metals

Table 3-54 lists the amount of particulate and solids from the washings obtained in the cyclones and filter during tests 3 and 4. Particulate which settled out in the probe was combined with dust collected in the 10 m cyclones for analysis. The data on total quantities of particulate collected in the cyclones and filter, including the washings, were used to calculate metals emissions per cubic meter of gas emitted from the power plant stack. (For example, see Tables 3-62 through 3-64.)

3.7.3 Mass Spectrometry Analysis

Particulate and XAD-2 samples were analyzed for PNA's following the procedures described in Appendix E. Gravimetric and total chromatographic organics data for tests 3 and 4 are tabulated in Table 3-55. Results of LC fractionation analyses for test 3 are given in Table 3-56.

Total ion current chromatographs for the two XAD-2 extracts and XAD-2 blanks were obtained on the samples. In addition, background corrected mass spectra were developed for all large peaks and these were compared to the 26,000 spectra in the NBS library of mass spectra of common organics. Results, corrected for blank concentrations, are shown in Table 3-57.

The major species seen in XAD-2 extracts are polynuclear aromatics and phthalates esters. It is possible because of the ubiquitous nature of phthalate esters that contamination with plasticizers may have occurred.

The phthalates, especially bis(2-ethylhexyl), are present in the samples at higher levels than seen in laboratory blanks.

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TABLE 3-52

GULF POWER COMPANY, CRIST STATION
BOILER NO. 7 ICPES ANALYSIS OF COAL SAMPLES FOR METALS

	NBS Analysis of No. 1632 Coal	ICPES Analysis in PPM		
		Exxon Analysis of No. 1632 Coal Sample	Test No. 3 Coal	Test No. 4 Coal
Ag	<0.1	<.195	<.332	<2.62
Al	-	15,330	17,330	15,500
As	5.9	17.6	<4.6	<3.63
Ba	-	221	152	134
Be	1.5	1.77	1.88	1.58
Ca	-	4590	6420	4480
Cd	0.19	2.43	(1.27)	3
Co	-	2.65	2.52	(1.2)
Cr	20.2	13.1	19.5	13.7
Cu	18	17.6	11.4	13.4
Fe	8700	7420	25800	20,000
Hg	.12	23.8	<3.19	(7.55)
K	-	2100	2930	2590
Mg	-	1120	1030	768
Mn	40	38.7	72.1	48
Mo	-	(3.4)	11	10.2
Na	-	288	294	258
Nb	-	<.899	<1.53	<1.21
Ni	15	17.1	33.9	15.7
P	-	104	883	126
Pb	30	24.3	13	8.95
Pt	-	(3.97)	(9.18)	(3.85)
Sb	-	<2.92	<4.98	<3.93
Se	2.9	<4.12	17.9	<5.54
Si	32000	26,300	36,400	29,900
Sn	-	<1.8	<3.06	2.42
Ti	-	965	1030	910
Tl	.59	<2.02	<3.45	<2.72
U	1.4	4.72	<8.05	<6.35
V	35	32	35.3	28.3
Zn	37	34	54.9	47.4

< Means element not detected.
( ) Value may not be significant.

TABLE 3-53

COAL ANALYSES

-- Gulf Power Company - Crist Station, Boiler No. 7 --

Test No.	127/128	129	130	132	132A	133	134	135	137	151	152	153
Laboratory No.	9060608	9060613	9060606	9060605	9060610	9060612	9060611	9060607	9060609	-	-	-
Sample Source	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal	Composite Coal
Date	2/7/78	2/8/79	2/9/78	2/16/78	2/17/78	2/23/78	2/23/78	2/28/78	3/2/78	6/21/78	6/22/78	6/23/78
Test Conditions	Baseline	Baseline	Baseline	Baseline	Baseline	Baseline	Low NO_x	Baseline	Low NO_x	Low NO_x	Baseline	Low NO_x
Proximate Analysis												
Moisture (as analyzed)	5.59	7.61	6.57	6.66	5.96	5.25	5.12	5.99	5.94	8.48	7.64	8.07
Ash	16.13	15.05	11.75	11.51	10.90	12.39	12.54	11.37	12.26	12.45	16.48	14.32
Volatiles	34.08	32.67	33.51	32.63	34.09	31.95	32.66	33.12	32.97	34.47	33.00	33.43
Fixed Carbon	44.20	48.35	48.17	49.20	49.05	50.41	49.68	49.52	48.83	44.60	42.88	44.18
Sulfur	5.36	3.84	3.59	3.28	3.05	3.73	3.80	3.08	3.23	3.89	3.70	3.89
Btu/lb.	11,028	10,583	11,670	11,700	11,901	11,813	11,828	11,863	11,593	11,263	10,782	11,033
Hardgrove Grindability	-	-	-	-	-	-	-	-	-	-	-	-
Ultimate Analysis-As Analyzed												
C - %	60.56	59.02	64.87	64.99	66.04	65.58	65.29	65.89	64.87	62.18	59.62	61.61
H - %	4.26	4.17	4.49	4.53	4.57	4.47	4.51	4.51	4.37	4.37	4.27	4.27
S - %	5.36	3.84	3.59	3.28	3.05	3.73	3.80	3.08	3.23	3.89	3.70	3.39
N - %	1.02	1.04	1.17	1.07	1.09	1.18	1.16	1.20	1.08	1.14	1.12	1.12
Cl - %	-	-	-	-	-	-	-	-	-	0.08	0.05	0.05
O - %	7.15	9.28	7.48	7.99	8.58	7.50	7.31	8.08	8.48	7.41	7.12	7.35
Ash - %	16.13	15.05	11.75	11.51	10.90	12.39	12.54	11.37	12.26	12.45	16.48	14.32
Btu/lb. - %	11,028	10,583	11,670	11,700	11,901	11,813	11,828	11,863	11,593	11,263	10,782	11,033
Ash Elements												
P_2O_5 - %	0.28	0.22	0.17	0.17	0.19	0.31	0.29	0.24	0.24	0.19	0.27	0.28
SiO_2 - %	42.90	47.20	45.08	47.28	47.85	42.81	42.01	45.70	45.45	40.25	45.63	44.93
Fe_2O_3 - %	29.31	20.98	22.27	19.17	16.92	24.49	25.53	18.48	20.34	27.58	18.08	18.02
Al_2O_3 - %	19.48	19.23	18.01	17.21	19.18	19.15	18.39	18.60	20.46	18.38	21.21	21.05
TiO_2 - %	0.91	0.91	0.87	0.89	0.93	0.94	0.94	0.91	0.95	0.81	0.90	0.89
CaO - %	1.72	3.50	5.09	4.13	3.88	3.89	3.85	4.45	4.22	3.68	3.84	3.85
MgO - %	0.65	0.95	0.80	0.85	0.80	0.79	0.81	0.84	0.80	0.87	1.01	1.03
SO_3 - %	1.89	4.07	5.95	4.90	4.77	4.30	4.16	5.48	5.13	4.83	4.63	4.76
K_2O - %	2.06	2.61	2.41	2.49	2.37	2.27	2.02	2.31	2.34	2.35	2.67	2.65
Na_2O - %	0.44	0.50	0.68	0.36	0.62	0.48	0.55	0.59	0.52	0.48	0.31	0.32
Total - %	99.64	100.17	101.33	97.45	97.51	99.43	98.55	97.60	100.45	99.54	98.68	97.91
Ash Fusion Temperature, °F												
Reducing - I.D.	1965	1935	1950	1935	1975	1960	1950	1955	1950	-	-	-
- H-W	1990	1960	2010	2035	2000	1990	1980	2050	1965	-	-	-
- H-1/2W	2010	1975	2030	2055	2020	2010	2000	2065	1975	-	-	-
- Fluid	2100	2015	2090	2105	2080	2060	2055	2135	2030	-	-	-
Oxidizing - I.D.	2320	2360	2325	2305	2300	2370	2370	2275	2310	-	-	-
- H-W	2370	2440	2360	2375	2380	2450	2430	2365	2480	-	-	-
- H-1/2W	2430	2490	2430	2450	2440	2470	2460	2450	2500	-	-	-
- Fluid	2525	2550	2475	2470	2500	2530	2510	2460	2515	-	-	-

TABLE 3-54

MASS OF MATERIAL COLLECTED IN SASS CYCLONES
(Reported in Grams)

GULF POWER COMPANY
CRIST STATION, NO. 7 BOILER

	Test No. 3 SASS 6/22/78	Test No. 4 SASS 6/23/78
10 µm Cyclone & Probe	10.78093	48.20833
10 µm Wash	1.64931	0.39421
10 µm Total	12.43024	48.60254
3 µm Cyclone	16.89219	35.58187
3 µm Wash	0.48543	0.43547
3 µm Total	17.37762	36.01734
1 µm Cyclone	5.38432	12.70445
1 µm Wash	0.14361	0.55059
1 µm Total	5.52793	13.25504
Filter	1.53143	2.79013
Filter Housing Wash	0.15808	0.11090
Filter Total	1.68951	2.90103

TABLE 3-55

GULF POWER COMPANY - CRIST STATION
NO. 7 BOILER

(PULVERIZED COAL FIRING)

ORGANICS ANALYSIS REPORT

Test No.	Test Date	Sample Type	Weight of Sample Extracted (g)	Gravimetrics (mg)	T.C.O. (mg)	Total Organics (mg)	Total mg/kg
3	6-22-78 (Baseline)	XAD-2 Resin: Inlet	110.20	6.2	178.0	184.2	1671.5
		Fly Ash: 10 μm + 3 μm inlet	4.46144 (10 μm Fly Ash) 5.78863 (3 μm Fly Ash)	<0.1	0.9	87.8	
4	6-23-78 (Low NO_x)	XAD-2 Resin: Inlet	109.30	32.2	22.7	54.9	502.3
		Fly Ash: 10 μm + 3 μm Inlet	5.78777 (10 μm Fly Ash) 4.29115 (3 μm Fly Ash)	<0.1	<0.1	<0.1	<9.9

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TABLE 3-56

GULF POWER COMPANY - CRIST STATION
BOILER NO. 7

(PULVERIZED COAL FIRING)

REPORT OF LC FRACTIONATION RESULTS

TEST SITE: Pensacola, Florida

SAMPLE : Test 3, Inlet XAD-2 Resin

EQUIVALENT TOTAL SAMPLE QUANTITIES				
Fraction	TCO, mg	GRAV, mg	Total, mg	Total mg/m^3
LC 1	<0.01	10.45	10.45	0.56
LC 2	<0.01	0.10	0.10	0.01
LC 3	<0.01	5.00	5.00	0.27
LC 4	<0.01	0.95	0.95	0.05
LC 5	<0.01	0.45	0.45	0.02
LC 6	<0.01	8.10	8.10	0.43
LC 7	<0.01	3.10	3.10	0.17

Quantity taken for LC: 4 mls/10 mls
mg loaded: TCO, 71.2
GRAV, 2.5

COMMENTS:

1. Based on total sample volume of 18.7 m^3.

2. Sample values reported are corrected for blanks.

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TABLE 3-57

GULF POWER COMPANY - CRIST STATION
BOILER NO. 7

(PULVERIZED COAL FIRING)

ORGANICS DETECTED IN PENSACOLA, FLORIDA XAD EXTRACTS

Compound	Concentration mg/m^3 a,b	
	Baseline Test 3	Low NO_x Test 4
Phenanthrene/anthracene	0.0001 (0.0005)	0.0005
Bis(2-ethylhexyl)phthalate	0.04	0.01
Fluoranthene	0.0002(0.0004)	0.0001
Pyrene	0.0002(0.0005)	0.0002
Naphthalene	(0.0002)	0.0006
Fluorene	0.0001	--
Silicones	--	0.005
Dichlorobenzene	--	0.0002
Dimethyl phthalate	--	0.0003
Chrysene/benz(a)anthracene	--	0.0001
Benzoic acid	--	0.05

a. Values in parentheses were measured after liquid chromatographic separation of the total XAD extract, combination of fractions 2 and 3 and GCMS analysis.

b. Concentrations based on
Test 3 -- 18.7m^3 sampled
Test 4 -- 26.9m^3 sampled

This may be due to contamination. Test 4 inlet XAD-2 extract was unusual in that the major components were silicones and benzoic acid. These materials were not seen in blanks.

After liquid chromatographic separation, Test 3 fractions 2 and 3 were analyzed for polynuclear aromatics (PNA's). The results (Table 3-57) indicate that the same compounds were detected in the whole samples. However, the measured quantities differ by factors of two to five. All of the quantities measured in these experiments are close to the detection limit for the instrument.

In Test 3 Inlet LC Fraction 1, a large amount of molecular sulfur was observed. No other species could be detected in any LRMS analysis.

A comparison of the data in Table 3-57 reveals no adverse side effects due to low-NO_x firing conditions (test 4) compared to baseline (test 3) on PNA's.

Tables F-1 through F-19 present IR analysis data of column fractions with assignments of the compound classes which were found.

Table 3-58 lists results of boron analyses by the Circuman Method. Data on leachable ions by neutral and acid extraction are presented in Tables 3-59, 3-60 and 3-61.

Each section of the SASS train was analyzed for trace metals which collect on the particulate (in the 10, 3, and 1 micrometer cyclones and the final filter), in the XAD-2 Amberlite adsorbent and condensate, in the hydrogen peroxide solution in the first impinger, and in impingers 2 and 3 containing ammonium persulfate and silver nitrate solutions. Table 3-62 presents a summary of the trace metal data obtained in tests at Crist No. 7. These results were obtained by summing the metal data for all sections of the SASS train (Tables 3-63 and 3-64). Of the 13 EPA priority pollutant metals, it may be seen that chromium, copper, nickel, lead, titanium and zinc were found in the highest concentrations. The levels of arsenic, beryllium, cadmium, mercury, antimony and selinium were present in lower concentrations. Data are also presented on 12 other elements with iron, uranium and zirconium present at levels greater than 20,000 $\mu g/m^3$. Comparing metal concentrations for test 3, taken under baseline operating conditions, to test 4, obtained under low-NO_x operation, it may be seen that there are no major differences or adverse effects of low-NO_x firing on these concentrations.

In the tables, the sample is identified according to the module of the SASS train in which it was trapped. The fly ash samples are designated by particle size (1, 3, or 10 μm). Other SASS samples are designated: filter, XAD-2 resin, first impinger

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TABLE 3-58

BORON ANALYSIS

CURCUMIN METHOD

Acurex ID No.	Sample	Concentration
78-0211	3-Inlet-XAD-2 Resin	39 μg/g
78-0268	4-Inlet-XAD-2 Resin	<20 μg/g
78-0212	3-Inlet-1 μm Fly Ash	330 μg/g
78-0213	3-Inlet-3 μm Fly Ash	680 μg/g
78-0214	3-Inlet-10 μm Fly Ash	490 μg/g
78-0285	4-Inlet-1 μm Fly Ash	390 μg/g
78-0287	4-Inlet-3 μm Fly Ash	310 μg/g
78-0286	4-Inlet-10 μm Fly Ash	370 μg/g
78-0210	3-Inlet-First Impinger	29 μg/g
78-0279	4-Inlet-First Impinger	30 μg/g

TABLE 3-59

LEACHABLE IONS -- NEUTRAL EXTRACTION

	Chloride Cl- µg/m^3	Fluoride F- µg/m^3	Cyanide CN- µg/m^3	Ammonium NH$_4$+ µg/m^3	Nitrate NO$_3$- µg/m^3	Sulfate SO$_4$= µg/m^3
Test 4 -- Inlet 10 µm Fly Ash	63.2	5.2	<0.2	16.1	15.4	469.2
Test 4 -- Inlet 3 µm Fly Ash	31.1	2.4	<0.13	0.4	1.9	379.6
Detection Limits	0.5	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.05 ppm

TABLE 3-60

LEACHABLE IONS -- ACID EXTRACTION

	Chloride Cl^- $\mu g/m^3$	Fluoride F^- $\mu g/m^3$	Cyanide CN^- $\mu g/m^3$	Ammonium NH_4^+ $\mu g/m^3$	Sulfate $SO_4^=$ $\mu g/m^3$
Test 4 -- Inlet 10 μm Fly Ash	9.0	7.2	<0.2	15.4	556.7
Test 4 -- Inlet 3 μm Fly Ash	31.2	4.2	<0.13	3.4	368.7
Detection Limit	0.5 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.5 ppm

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TABLE 3-61

QUALITY CONTROL -- LEACHABLE IONS

Ammonuim, Fluoride, Cyanide All values calculated by method of known addition
Sulfate Four determinations -- average 95.2% recovery
Nitrate One determination -- 89.8% recovery
Chloride Two determinations -- average 100.1%

TABLE 3-62

SUMMARY OF METAL DATA ON STACK EMISSIONS*
($\mu g/m^3$)

		Test No. 3 (Baseline)		Test No. 4 (Low NO_x)	
Silver, Ag	13 EPA Priority Pollutants	NR	NR	-	NR
Arsenic, As		151.5	151.2	-	215
Beryllium, Be		28.1	28.1	-	45.7
Cadmium, Cd		2.01	2.01	-	22.8
Chromium, Cr		4363	4349	-	1153
Copper, Cu		249	249	-	369
Mercury, Hg		7.3	7.3	-	<19.9
Nickel, Ni		2702	2696	-	699
Lead, Pb		257	255	-	505
Antimony, Sb		39.9	38.2	-	49.6
Selenium, Se		52.4	52.2	-	67
Titanium, Ti		10,174	10,507	-	17,938
Zinc, Zn		1596	1542	-	3012
Barium, Ba		3727	3860	-	8152
Bismuth, Bi		< 8.3	<8.3	-	<12.7
Cobalt, Co		223	226	-	264.5
Iron, Fe		50,471	41,830	-	106,216
Manganese, Mn		2011	1931	-	3465
Molybdenum, Mo		386	386	-	292
Tellurium, Te		6.2	6.2	-	<6
Thallium, Th		< 791	791	-	<1477
Tin, Sn		11.7	11.7	-	18.2
Uranium, U		<402,549	<402,549	-	<321,648
Vanadium, Va		743	730	-	1063
Zirconium, Zr		<40,255	40,255	-	32,163

First Analysis
Second Analysis

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*Totals of data presented in Tables 3-64 and 3-65.

TABLE 3-63

ELEMENTAL ANALYSIS
(Baseline Operation) ($\mu g/m^3$)
(Test #3)

Lab ID #	78-0214		78-0213	78-0212	—	78-0210	78-0210	78-0209
Sample / Element	PF-3-I-10μ		PF-3-I-3μ	PF-3-I-1μ	PF-3-I-Filter	PF-3-I-XAD	PF-3-I-1st Impinger	P-3-I-2nd & 3rd Impinger
Antimony, Sb	1.9	0.7	0.8	4	29	< 3.2	< 0.2	< 0.3
Arsenic, As	17.9	18.6	67	38	22	< 3.7	2.5	< 0.4
Barium, Ba	864	997	2044	562	70	150	< 37.4	
Beryllium, Be	6.6	6.6	12	4.7	1.4	< 3.2	< 0.2	
Bismuth, Bi	< 2.0	< 2.0	< 2.8	< 0.9	< 0.2	< 2.1	0.3	
Cadmium, Cd	1.9	1.9	4.6	4	5.1	< 0.1	< 0.01	
Chromium, Cr	273	259	149	89	23	86	3743	
Cobalt, Co	22	25	31	18	1.8	< 107	42.8	
Copper, Cu	51	.51	75	35	7.5	< 0.2	80	
Iron, Fe	19277	10,636	19515	6208	903	23	4545	
Lead, Pb	53	51	121	65	7.2	8.6	1.8	
Manganese, Mn	592	512	688	287	38	10.2	396	
Mercury, Hg	0.3	< 0.3	< .37	< 0.1	< 0.1	< 4.3	2.1	< 0.5
Molybdenum, Mo	8.6	8.6	9.3	4	44	< 53.5	267	
Nickel, Ni	186	180	112	44	18	< 42.8	2299	
Selenium, Se	1.3	1.1	1.2	0.4	0.9	< 1.6	47	
Tellurium, Te	< 0.4	< 0.4	< 0.56	< 0.2	0.3	< 4.3	< 0-4	
Thallium, Th	< 266	< 266	372	< 118	1.1	32.6	1.0	
Tin, Sn	< 0.7	< 0.7	< 0.9	1.2	0.9	< 2.1	5.9	
Titanium, Ti	2725	3058	4275	1951	126	< 26.7	< 1070	
Uranium, U	< 19942	< 19942	< 27879	< 8868	< 3614	< 320856	< 21390	
Vanadium, Va	153	140	288	142	99	< 53.5	7.0	
Zinc, Zn	366	312	585	355	49	< 16.0	225	
Zirconium, Zr	< 1994	< 1994	< 2788	< 887	< 361	< 32086	< 2139	

TABLE 3-64

ELEMENTAL ANALYSIS
(Low NO_x Operation) (μg/m³)
(Test #4)

Lab ID # Sample Element	78-0286 PF-4-I-10μ	78-0287 PF-4-I-3μ	78-0285 PF-4-I-1μ	— PF-4-I-Filter	78-0268 PF-4-I-XAD	78-0279 PF-4-I-1st Impinger	78-0278 PF-4-I-2nd & 3rd Impinger
Antimony, Sb	< 0.5	2.5	2.3	42	<1.9	<0.2	< 0.2
Arsenic, As	47	86	59	18	<2.2	2.1	0.7
Barium, Ba	2891	3213	1380	59	520	89	
Beryllium, Be	18.1	16	8	1.7	<1.9	0.04	
Bismuth, Bi	<5.4	< 4	<1.5	<0.2	<1.1	0.5	
Cadmium, Cd	4.0	6.6	5	6.4	0.4	0.4	
Chromium, Cr	452	241	118	18	23	301	
Cobalt, Co	79.5	55	24	3.0	74	29	
Copper, Cu	132	111	54	8.7	7.4	56	
Iron, Fe	57817	29457	11826	1726	929	4461	
Lead, Pb	150	214	123	10	5.9	1.6	
Manganese, Mn	1283	1259	591	0.03	1.4	331	
Mercury, Hg	< 0.7	< 0.5	<0.2	<0.06	<2.6	<0.8	< 15
Molybdenum, Mo	12.6	11	5.4	55	< 30	178	
Nickel, Ni	343	161	74	5.6	< 26	89	
Selenium, Se	3.1	7.2	1.2	1.9	1.5	52	
Tellurium, Te	<1.1	< 0.8	<0.3	0.5	< 3	<0.3	
Thallium, Th	<723	< 536	<197	1.1	19	<0.7	
Tin, Sn	<1.8	2.7	5	6.5	<1.1	<1.1	
Titanium, Ti	7769	5490	3301	248	<15	<1115	
Uranium, U	<54204	< 40168	<14783	<4314	<185874	<22305	
Vanadium, Va	379	348	187	106	<33	10	
Zinc, Zn	614	1473	542	194	<11	178	
Zirconium, Zr	<5420	< 4017	<1478	<431	<18587	<2230	

and second and third impingers. All samples are designated with either the letter "I" or the word "Inlet", meaning that they came from the SASS train leading to the electrostatic precipitator. PF stands for Pensacola, Florida.

Metal analyses broken down by sections of the SASS train for tests 3 and 4 are summarized in Tables 3-63 and 3-64. The twenty-four elements in these tables were analyzed by atomic absorption. Corrections were made for blanks and matrix interferences. When comparisons are made of the metal concentrations in tests 3 and 4 for each section of the SASS train, the conclusion reached is that low-NO_x operation has little or no effect on the results. In effect, the distribution of the metal concentrations essentially is the same for baseline and low-NO_x firing conditions with variations between values mainly influenced by the differences in coal quality fired during each test. These results duplicate conclusions from previous SASS train tests leading to the preliminary conclusion that low-NO_x combustion modifications, at the levels practiced in these tests, have no significant effect on trace metal emissions. Low-NO_x emissions are essentially the same as for baseline operation.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Gaseous Emission Measurements

NO_x and other emissions were measured while combustion modifications were used to decrease NO_x emission rates. With the exception of CO, no other gaseous emission was seen to be significantly affected by such combustion modifications. Furthermore, CO was easily measured and controlled by use of a CO monitor. Such monitoring was a useful tool in finding the minimum acceptable excess air for NO_x control.

Four methods of NO_x control were investigated at Crist No. 7. They were:

- Secondary air register settings (i.e. air feed distribution)
- Firing patterns (i.e. fuel feed distribution)
- Load
- Total air flow (excess air)

Some of these were more effective than others in reducing NO_x emissions. Adjustment of the secondary air registers was perhaps the least effective of all control methods tried. No relationship was evident between secondary air register settings and NO_x emissions; thus helping to confirm that the main purpose of the register is as a swirl-inducing device, not a dampler. Reducing the register setting to a more closed position may result in a decreased air flow through it, but such closing increases swirl and turbulence. The increased swirl may be counterproductive to any effects which might decrease NO_x by way of slight reductions in air flow. The effects of other control methods are discussed below.

Firing mode had a clear effect on NO_x as is easily seen in Figure 3-1 which generally shows that NO_x decreases as the degree of staging (firing mode ID number) increases.

Staging is an effective means of NO_x control because it reduces fuel NO_x formation by decreasing oxygen availability to the fuel-bound nitrogen in the early part of the flame. Sufficient reduction in stoichiometry near the burner will also depress the flame temperature thereby also lowering the amount of thermal NO_x formed.

One representation of the effect of staging on NO_x emissions is shown in Figure 3-5. Here the reader can see that NO_x emissions decrease as fuel feed to the top burners is cut back. However, in Figure 3-5, the actual NO_x reduction obtained due to staging is somewhat masked by the effects of decreased load and decreased air.

Load reduction is not generally considered for NO_x control since it is a very expensive control technique. Generally, NO_x emission rates decrease as boiler load (and thus fuel consumption rate) decreases because the accompanying drop in fuel consumption rate results in a cooler flame.

Figure 3-2 shows that load reductions are most effective (steepest slope) when load is initially high. As load is reduced, the advantage of further load reduction becomes less attractive. (The curves on the left side of Figure 3-1 become less steep.)

Reduction of excess air to the design value or lower for boilers routinely operating at high excess air will reduce NO_x emissions. This is seen in Fig. 3-4 which shows NO_x decreasing as excess air is decreased.

Of course one cannot decrease the amount of excess air too much, or combustion will be incomplete, resulting in increased carbon on ash, decreased boiler efficiency, and increased particulate emissions (smoke and soot). Some of this inefficiency is recovered because by decreasing the amount of excess air, the amount of energy needed to heat the excess air is also reduced and the amount of waste heat going up the stack is decreased.

As excess air is decreased, the first short term adverse side effect is an increase in CO emissions. This happens before the onset of more serious problems such as soot formation. Hence, CO emissions can be used as a guide to NO_x control through decreased air flows (only CO emission rates below 200 ppm are acceptable).

When decreasing excess air for NO_x control, it is desirable to stop the decrease when the first "swings" or "spikes" in the CO detector are observed. Such spikes are probably caused by one or more unbalanced burners which begin to "flicker" before the other burners do. The boiler manufacturer recommends that excess air then be increased to provide an operating safety margin.

Although regulation of excess air is a very effective method of NO_x control, not all boilers are equipped with CO monitors, and in those cases, significantly deep reductions in excess air flow are not always possible as a method of NO_x control.

The following summarizes the conclusions and recommendations pertaining to emissions.

Conclusions

- At full load, flue gas NO_x concentration is typically 926 ppm at "baseline" (has been as high as 1200 ppm), and 723 ppm at "low-NO_x". (Corrected to 3% O_2, dry basis.)
- NO_x emissions rates near full load are decreased by more than 20% without immediate or otherwise observed adverse side effects through optimum use of existing control mechanisms. (No retrofit required.)

- NO_x controls have the potential to increase CO emissions, but this can be controlled.

- Some boiler operations may preclude the use of "low-NO_x" parameters (e.g., low load, start-ups, upsets).

- NO_x emissions could be decreased at utility boilers through use of the following combustion modifications:

  - Decrease excess O_2 until flue gas CO increases rapidly. (Keep burners in tune to minimize CO flicker.) Then increase excess air to obtain suitable operating margin.

  - The air/fuel ratio of the top elevation of burners should be as high as possible, even to the point of feeding only air (no fuel) through the top burners simulating over-fire-air ports when load demand allows.

- To aid in reducing excess air to optimum safe levels, boilers must be equipped with a CO monitor.

Foster Wheeler Energy Corp., the manufacturer of the Crist No. 7 steam generator, does not recommend staged firing (either with overfire air or burner biasing) on pre-NSPS units. Instead, to reduce NO_x emissions on existing steam generators, Foster Wheeler recommends retrofitting low-NO_x burners. FWEC feels that such low-NO_x burners can produce larger NO_x reductions than can be obtained by staged firing and this can be done without introducing reducing atmospheres to the burner zone water-wall tube surfaces. Also, with new low-NO_x burners, unit operation and flexibility would not be impaired as is the case with the methods used during the Crist 7 tests. Low-NO_x burners would allow the unit to achieve full load and not require pulverizer load capacity to be dedicated to low NO_x firing.

4.2 Conclusion and Recommendations on Corrosion Measurements

Considerable experience and knowledge has been developed through this comprehensive, long-term corrosion study conducted on Crist No. 7 boiler by Exxon Research and Foster Wheeler with the cooperation and support of the Gulf Power Company. In many ways it was a pioneering effort, since this was the first long-term corrosion study on a high sulfur coal fueled, wall-fired boiler that utilized three methods of measuring corrosion (probe coupons, wall tube test panels and ultrasonic furnace wall tube measurements) at several levels.

The conclusions reached on this boiler will not, of course, apply to all large wall-fired boilers fueled with high sulfur coal. Fuel characteristics, burner design, furnace design (number of burners, size and spacing; heat release per square foot of furnace area, etc.), and boiler operation (load, slag removal procedures, burner register settings, excess air level) will differ from boiler to boiler and each factor might have a significant effect on furnace wall tube fireside corrosion. Additional comprehensive, long-term corrosion test programs to determine furnace tube wall corrosion rates by actual tube wall thickness measurements are required to establish whether fuel rich, staged firing of different coal types in different boiler design types produces abnormal corrosion rates. At present an EPA sponsored program involving two-year tests on three modern boilers designed to meet the NSPS standards for NO_x emissions is underway. This program, involving boilers designed by Babcock and Wilcox and Combustion Engineering companies, should help to answer many of the remaining questions pertaining to tube wall corrosion.

As discussed in detail in Section 3, the staged combustion operation to reduce NO_x emissions on this boiler resulted in increased tube wall corrosion rates on the furnace walls within the burner elevation as shown by test panel, ultrasonic furnace wall and one-day duration probe coupon measurements. The average loss measured on the furnace wall tubes within the burner area was 5±1 mils during the 12-month low-NO_x operating period compared to 2.1 ± 0.6 mils for the furnace non-burner area. Of the four furnace walls, the left sidewall burner area tubes experienced the largest average loss (6.2 mils). FWEC has pointed out (Appendix H) that, for the 12 month low-NO_x period, significant furnace wall corrosion occurred during only the first two thirds of the period. Corresponding baseline operation corrosion average measurements on furnace tubes were 1.7 mils (4 mils per year) for the entire furnace burner area and 0.6 mils (1.4 mils per year) for the left wall burner area. Test panel corrosion measurements generally supported the conclusions reached for the actual furnace wall measurements. Three panels within the burner area experienced an average loss of 10 mils vs 0 mils loss for three panels located outside the burner area during the 12-month low-NO_x operation. During baseline operation, the average loss on panels within the burner area (2.6 mils or 6.2 mils/year) was not significantly different than the average loss of panels outside the burner area (2.2 mils or 5.3 mils/year).

The higher corrosion rate due to staging occurred in the region of the sidewalls where the increase had been predicted: near the sidewalls' centerlines between the upper two burner elevations. During the low-NO_x operating period, staging was recommended as a standard operating practice when conditions allowed it. Concurrently, burners had to be periodically taken in and out of service for routine planned pulverizer maintenance (grinding element replacement, coal conduit elbow repair, etc.). Since the registers of the out-of-service-burners remained open, the lower furnace was at oxidizing conditions when any of the lower four mills (two on each side) were out of service, whether for planned maintenance, or because of low load demand. During normal operations when all mills were available, load demand was such that on many occasions mills could not be biased to yield a reducing atmosphere in the burner zone. These occurrences meant that staging was not used as frequently or as effectively as would have been the case on a boiler designed for staged combustion. Consequently the ten mil/year corrosion rate for the three panels in the burner zone during low-NO_x operation might have been even higher if staging had been used more frequently at the Crist No. 7 boiler.

Some of the data (for example the low corrosion rate on Panel No. 5, which was the closest panel to the rear wall) seem to indicate that the curtain air (installed on the rear wall) may have played a part in reducing the corrosion rate. However, the tube wall data (Tables 3-27 and 3-28) do not strongly support this. Furthermore, the manufacturer claims that the curtain air was installed to correct a slagging problem and was not expected to have an effect on corrosion rates.

The data also seem to indicate that for the materials tested in panels as well as probes, corrosion rate was not significantly dependent on the type of steel used, and, the corrosion rate on test coupons decreased significantly with the period of exposure (measured from 24 hours to 1000 hours) in line with other researchers' experiences. Assuming that furnace tubes likewise experience decreasing corrosion rates with time, the corrosion rates experienced on Crist No. 7 boiler during extended low-NO_x operation would not appear to appreciably reduce the expected useful life of the furnace tubes.

These numbers (including data from Tables 3-27 and 3-28) are summarized in Table 3-65.

TABLE 3-65

WALL MEASUREMENT SUMMARY

Metal loss in mils (or mils per year)

	Non-Burner Zone (All Walls)	Burner Zone (All Walls)	Burner Zone (Left Wall)	Furnace Average
Baseline (5 months)	2.6 mils (6.2 mils/yr)	1.7 mils (4.0 mils/yr)	0.6 mils (1.4 mils/yr)	2.2 (5.2)
Low-NO_x (12 months)	2.1 mils (2.1 mils/yr)	5 mils (5 mils/yr)	6.2 mils (6.2 mils/yr)	3.4 (3.4)

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(2) H. D. Kerr, T. J. Kulle, et al. "Effects of Nitrogen Dioxide on Pulmonary Function in Human Subjects: An Environmental Chamber Study," (August 1979) Abstract found in the Air and Water Conservation Section of API Abstracts/Literature. American Petroleum Institute, New York, NY, Vol. 27, No. 6, Pg. 9, Feburary 11, 1980.

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(5) Third Symposium on Stationary Source Combustion, sponsored by U.S. Environmental Protection Agency, March 5-8, 1979, San Francisco, California, "Introductory Remarks." EPA No. EPA-600/7-79-050e (NTIS No. PB 298174/AS).

(6) United States Environmental Protection Agency (EPA), Office of Air Programs, Contract CPA 70-90.

(7) A. R. Crawford, E. H. Manny and W. Bartok, "Field Testing: Application of Combustion Modification to Control NO_x Emissions from Utility Boilers," pg. XIII. Exxon Research and Engineering Company, EPA Report No. EPA-650/2-74-066 (NTIS No. PB 237-344/AS) June, 1974.

(8) A. R. Crawford, E. H. Manny and W. Bartok, "Control of Utility Boiler and Gas Turbine Pollutant Emissions by Combustion Modification - Phase I," pg. 1, Exxon Research and Engineering Company, EPA Report No. EPA-600/7-78-03a (NTIS No. PB 281078) March, 1978.

(9) Contract #CPA 70-90 (see Reference No. 6).

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(12) "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (second edition)." EPA - 600/7-78-201, October, 1978 (NTIS No. PB 293795).

(13) R. L. Burrington, J. D. Cavers, A. P. Seeker, "Overfire Air Technology for Tangentially Fired Utility Boilers Burning Western U.S. Coal," pgs. 301-311, Combustion Engineering Inc., Power Systems Division, EPA Report No. EPA-600/7-77-117 (NTIS No. PB 277 012), October 1977.

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(15) John W. Tukey, "A Re-examination, from Statistical and Some Measurement Viewpoints of the Corrosion Measurements on the Widow's Creek, No. 5 Boiler." Unpublished report to Industrial Environmental Research Laboratory of EPA from the Department of Statistics, Princeton University. (1977).

(16) John W. Tukey, "Statistical Considerations Important in Analyzing Measurement Changes in Waterwall Tube Thickness", pgs. 79-92, Proceedings of the Second Stationary Source Combustion Symposium, Volume 5, Addendum. EPA-600/7-77-073e, NTIS No. PB 274897/AS, July 1977.

(17) Much of the SASS analysis (reported in section 3.7) and methodology (Appendix E) was contributed by Acurex Corporation, from work performed for EPA under contract No. 68-02-3188.

SUGGESTED ADDITIONAL READING ON CORROSION CHEMISTRY:

Neither corrosion chemistry nor slag analysis or formation mechanisms are presented here at this time. However, the interested reader may wish to obtain one or more of the publications listed below for more information on the subject.

o T. F. Wall, A. Lowe, L. J. Wibberley, and I. McC. Stewart "Mineral Matter in Coal and the Thermal Performance of Large Boilers," Journal of Prog. Energy Combustion Science, Volume 5, pgs. 1-29 c Pergamon Press Ltd., 1979, Great Britain.

o A. J. Blazewicz, and M. Gold, "High Temperature Gas Side Corrosion in Coal Fired Boilers," Babcock & Wilcox Co., as summarized by W. Reid. Contributed by the Fuels Division of the American Society of Mechanical Engineers for presentation at the Winter Annual Meeting, New York, NY, December 2-7, 1979, ASME Publication #79-WA/FU-6.

- D. W. C. Baker, M. J. Fountain, A. B. Hart, K. A. Hay, D. R. Holmes, P. J. Jackson, J. Jarman, C. W. King, J. W. Laxton, D. Mortimer and L. H. Toft, "The Control of High Temperature Fireside Corrosion (second edition)," Central Energy Generating Board, London, England, EC1A 7AU, ISB No. 0-902543-45-8, pre-1977.

- G. F. Barcikowski, S. S. Blackburn, G. P. Hammer, D. A. Harris, D. G. Milligan, and W. R. Sylvester, "Locate Problems in Radiant and Convective Sections early to Improve Availability," Combustion Engineering Inc., Steam Generation, *Power Magazine*, March, 1978.

- I. M. Rehn (principal investigator), "Corrosion Problems in Coal-Fired Boiler Superheater and Reheater Tubes Fireside Corrosion," Foster Wheeler Development Corporation, 12 Peach Tree Hill Road Livingston, New Jersey 07039, prepared for the Electric Power Research Institute, CS-1653, Research Project 644-1, November, 1980.

- F. T. Greene, J. E. Beachey, and T. A. Milne, "Direct Sampling and Characterization of Gaseous Species Responsible for Fireside Corrosion in Fossil Fuel-Fired Systems," Midwest Research Institute (MRI), Annual Report - Phase I, Energy Research and Development Administration, U.S. Dept. of Energy, Report, ERDA-FE-2288-4, prepared under Contract No. EX-76-C-01-2288, August 22, 1977.

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Appendix A

Program Schedule

An all day planning meeting of Exxon Research and Foster Wheeler on January 8, 1976, followed by a meeting of Exxon Research and Professor John Tukey (Princeton University and Bell Telephone Labs), a statistical consultant, preceded the broader meeting at Gulf Power Headquarters on February 7, 1976 where final agreement on the details for the Phase I* test program and the general procedures and schedule for Phases II, III and IV* were obtained from EPA, Exxon Research, Foster Wheeler and Gulf Power representatives.

Following completion of Phase I (February 9-16, 1976), Phase II (February 16-17, 1976) and Phase III (February 18-March 19, 1976) test programs, a second broad, planning field meeting (EPA, Exxon Research, Foster Wheeler and Gulf Power representatives) was held on April 21, 1976. This meeting had the following objectives: (1) review Crist No. 7 Phases I, II, and III test results; (2) review objectives and plans for Phase IV - long-term corrosion test program; (3) determine "best" alternative test program considering economic constraints, boiler overhaul schedules and technical requirements, and (4) visit Crist station site to finalize test panel, probe and gas sample port location. The major change in the test program decided at the 4/21/76 meeting was to provide for a 5-month sustained baseline operating test followed by a sustained 6-month "low-NO_x" operating period (with ultrasonic furnace wall tube thickness measurements at the beginning and end of the baseline operation and middle and end of the "low-NO_x" operating period). The prime reasons for including a baseline operating period was the desirability of including "control" measurements as well as allowing full load operation during the summer peak loads.

In the period of October, 1976 through January, 1977, a number of operating problems (including pulverizer overhauls, furnace tube failures, excessive cold weather, etc.) delayed the start of sustained "low-NO_x" operation until February, 1977. Subsequently, it was mutually agreed to extend the "low-NO_x" operation until the normal spring outage in 1978, since the unit came offline in July 1977 due to a generator problem. The final low-NO_x operating period turned out to comprise a total of 12 months.

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*Phases I, II, III, and IV are explained in Section 2.2.

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APPENDIX I

SUMMARY OF FLUE GAS COMPOSITIONS

TEST #		TEMP. (C)	O_2 (PCT) (MEAS)	NO_x (CHEMI) (PPM)	NO_x (CHEMI) (PPM)	NO (NDRI) (PPM)	NO_2 (PPM)	CO (PPM)	CO_2 (PCT)	SO_2 (PPM)	HC (PPM)
1		0.	4.35	914.	893.	871.	21.	16.	15.46	0.	5.
1	A	419.	3.54	757.	748.	719.	12.	15.	15.24	0.	14.
1	B	432.	5.24	865.	845.	811.	21.	14.	15.78	3076.	13.
1	C	460.	5.67	813.	799.	742.	14.	12.	15.35	2841.	11.
1	D	415.	6.14	808.	766.	744.	21.	45.	14.72	8331.	61.
1	E	0.	2.92	690.	888.	669.	12.	315.	15.48	6853.	0.
1	F	0.	6.97	510.	496.	540.	270.	30.	14.06	9496.	0.
1	G	0.	9.44	536.	522.	516.	104.	29.	14.11	8086.	0.
2		0.	3.24	797.	783.	768.	11.	15.	15.31	0.	5.
2	A	429.	2.15	696.	688.	649.	8.	37.	15.82	0.	3.
3		428.	3.63	811.	796.	761.	13.	14.	15.94	2941.	6.
3	A	432.	4.88	942.	919.	894.	17.	23.	15.21	0.	0.
4		429.	2.57	702.	695.	670.	8.	154.	16.01	2869.	6.
4	A	418.	3.36	767.	757.	736.	8.	18.	14.81	0.	6.
4	C	0.	2.71	657.	645.	636.	13.	332.	15.28	6681.	0.
4	D	0.	2.53	591.	560.	622.	10.	271.	15.28	6681.	0.
4	E	0.	2.56	520.	507.	558.	10.	316.	15.24	6634.	0.
7		429.	5.34	654.	633.	821.	24.	26.	14.82	3078.	30.
7	A	429.	4.22	667.	633.	663.	12.	12.	15.47	3127.	12.
8		419.	3.33	746.	735.	712.	13.	18.	15.56	2984.	9.
8	A	414.	2.07	559.	553.	534.	5.	45.	15.38	2777.	11.
11		414.	6.66	720.	705.	713.	17.	15.	15.71	3139.	11.
11	A	426.	4.69	548.	542.	548.	9.	12.	15.47	3142.	12.
11	B	410.	5.85	669.	651.	645.	16.	16.	14.63	3404.	29.
11	C	412.	6.49	714.	693.	697.	0.	46.	15.08	3195.	66.
12		396.	2.82	371.	368.	359.	3.	54.	15.62	3197.	7.
12	A	403.	2.50	412.	407.	412.	4.	71.	15.23	3221.	17.
17		374.	8.01	353.	348.	363.	3.	36.	14.79	3041.	75.
17	A	363.	8.79	520.	536.	536.	12.	33.	14.29	2593.	120.
18		360.	3.97	244.	241.	239.	3.	28.	15.39	2452.	0.
18	A	352.	6.32	327.	323.	326.	4.	39.	15.08	2195.	0.
23		348.	8.07	712.	694.	726.	20.	26.	15.22	2922.	27.
24		329.	4.92	483.	475.	474.	6.	18.	14.63	2976.	7.
31		0.	5.51	847.	826.	795.	18.	16.	15.50	0.	5.
32		413.	6.55	0.	0.	673.	0.	40.	14.25	2369.	82.
33		388.	6.24	441.	434.	450.	0.	25.	14.03	2775.	137.
34		342.	9.66	479.	467.	486.	12.	35.	13.62	155.	0.
50		0.	6.53	291.	289.	287.	0.	38.	16.05	0.	4.
51		454.	7.02	325.	322.	342.	0.	23.	13.95	0.	11.
52		395.	7.63	378.	376.	382.	0.	18.	14.55	0.	17.
53		399.	5.58	464.	454.	451.	0.	20.	15.80	0.	11.
54		394.	7.39	308.	304.	337.	0.	18.	14.25	0.	12.
55		363.	9.04	687.	670.	750.	0.	61.	13.90	0.	18.
56		0.	4.26	773.	763.	730.	0.	47.	15.16	0.	4.
56	8	0.	0.97	328.	650.	625.	0.	2185.	15.42	0.	5.
57		0.	4.28	689.	683.	650.	0.	13.	15.41	0.	34.
58		0.	4.36	455.	451.	450.	0.	36.	15.56	0.	8.
58	B	0.	1.92	0.	193.	195.	0.	4625.	15.40	0.	74.
59		0.	3.37	745.	741.	728.	0.	62.	15.28	0.	6.
60		0.	4.35	735.	730.	708.	0.	55.	15.45	0.	9.
61		0.	3.11	712.	708.	685.	0.	60.	15.13	0.	8.
62		0.	7.32	648.	640.	610.	0.	35.	14.21	0.	12.
63		0.	4.35	694.	689.	658.	0.	50.	15.32	0.	9.

NOT REPRODUCIBLE

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APPENDIX B (page 2 of 3)

SUMMARY OF FLUE GAS COMPOSITIONS

TEST #	TEMP. (C)	O_2 (PCT) (MEAS)	NO_x (CHEMI) (PPM)	NO_x (CHEMI) (PPM)	NO (NDRI) (PPM)	NO_2 (PPM)	CO (PPM)	CO_2 (PCT)	SO_2 (PPM)	HC (PPM)
64	0.	3.66	654.	648.	626.	0.	72.	15.13	0.	8.
65	0.	4.91	669.	664.	637.	0.	114.	15.42	0.	13.
66	0.	4.22	631.	624.	601.	0.	18.	14.69	0.	17.
67	0.	4.60	669.	663.	635.	0.	19.	15.55	0.	11.
68	0.	5.22	508.	501.	474.	0.	23.	15.25	0.	17.
69	0.	4.73	865.	859.	835.	0.	13.	15.27	0.	15.
70	0.	2.10	738.	733.	715.	0.	77.	15.25	0.	5.
71	0.	4.62	1218.	1200.	1217.	0.	21.	15.27	0.	13.
72	0.	4.17	1088.	1073.	1060.	0.	18.	14.84	0.	18.
73	0.	4.27	1193.	1177.	1155.	0.	19.	15.28	0.	11.
74	0.	6.62	898.	885.	869.	0.	22.	14.43	0.	13.
75	0.	5.71	755.	746.	739.	0.	25.	14.92	0.	12.
76	0.	6.37	765.	776.	736.	0.	42.	15.55	0.	24.
77	0.	5.58	737.	730.	722.	0.	48.	15.43	0.	13.
78	0.	6.34	970.	963.	923.	0.	86.	14.65	0.	27.
79	0.	7.30	853.	841.	820.	0.	284.	13.95	0.	19.
80	0.	6.37	852.	841.	814.	0.	24.	13.79	0.	20.
81	0.	3.69	893.	885.	867.	0.	18.	15.24	0.	9.
82	0.	4.13	930.	924.	0.	0.	14.	15.16	0.	18.
83	0.	5.47	805.	797.	0.	0.	27.	15.56	0.	16.
84	0.	3.55	804.	796.	774.	0.	17.	15.64	0.	2.
84 A	0.	3.12	747.	741.	740.	0.	16.	15.56	0.	2.
84 B	0.	3.77	801.	794.	0.	0.	16.	15.50	0.	4.
85	0.	3.37	824.	814.	802.	0.	16.	15.52	0.	8.
86	0.	5.52	629.	620.	576.	0.	58.	15.16	0.	13.
87	0.	5.69	855.	645.	636.	0.	79.	15.45	0.	8.
88	0.	5.72	758.	750.	736.	0.	17.	15.61	0.	31.
89	0.	3.48	530.	523.	494.	0.	193.	15.55	0.	26.
89 A	0.	3.32	537.	529.	0.	0.	43.	15.39	0.	11.
90	0.	3.48	530.	523.	494.	0.	314.	15.46	0.	15.
91	0.	4.20	800.	793.	823.	0.	17.	14.35	0.	0.
92	0.	3.55	847.	841.	824.	0.	16.	16.06	0.	0.
93	0.	4.29	815.	805.	799.	0.	16.	15.45	0.	0.
94	0.	3.16	815.	807.	772.	0.	19.	15.72	0.	0.
95	0.	3.01	713.	705.	684.	0.	1243.	15.37	0.	0.
96	0.	3.05	758.	746.	701.	0.	83.	15.57	0.	0.
97	0.	3.01	722.	715.	676.	0.	563.	15.53	0.	0.
98	0.	3.99	782.	776.	746.	0.	48.	15.19	0.	0.
100	0.	6.68	1001.	982.	967.	0.	19.	14.93	0.	7.
100 B	0.	5.12	1039.	1023.	974.	0.	9.	15.38	0.	11.
101	0.	3.62	832.	822.	822.	0.	49.	16.07	0.	6.
102	0.	5.32	756.	749.	743.	0.	35.	14.97	0.	9.
103	0.	1.77	537.	534.	532.	0.	266.	15.02	0.	6.
104	0.	4.55	772.	767.	760.	0.	12.	14.66	0.	8.
105	0.	2.39	645.	641.	623.	0.	34.	14.53	0.	13.
106	0.	5.46	653.	647.	623.	0.	13.	14.09	0.	15.
107	0.	2.13	447.	441.	469.	0.	255.	14.26	0.	10.
117	0.	5.53	390.	386.	370.	0.	12.	15.02	0.	8.
118	0.	1.79	225.	223.	225.	0.	540.	15.47	0.	5.
122	0.	5.79	1067.	1000.	947.	0.	13.	13.38	0.	6.
122 A	0.	5.02	1092	1075.	1059.	0.	17.	15.08	0.	11.
123	0.	4.37	1034.	1027.	1000.	0.	17.	15.20	0.	10.
124	0.	4.39	957.	962.	923.	0.	13.	14.88	0.	10.
125	0.	4.04	946.	0.	917.	0.	10.	15.54	0.	5.
126	0.	3.73	934.	0.	879.	0.	55.	14.33	0.	3.
127	0.	5.91	790.	0.	751.	0.	72.	13.34	0.	2.
128	0.	5.69	966.	0.	879.	0.	36.	12.96	0.	1.
129	0.	5.72	943.	0.	968.	0.	17.	13.75	0.	3.
130	0.	4.91	768.	0.	736.	0.	13.	15.28	0.	0.
131	0.	6.39	708.	0.	687.	0.	14.	14.74	0.	11.
132	0.	5.11	654.	0.	651.	0.	12.	15.06	0.	9.

NOT REPRODUCIBLE

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APPENDIX B (page 3 of 3)

SUMMARY OF FLUE GAS COMPOSITIONS

TEST #	TEMP. (C)	O_2 (PCT) (MEAS)	NO_x (CHEMI) (PPM)	NO_x (CHEMI) (PPM)	NO (NDRI) (PPM)	NO_2 (PPM)	CO (PPM)	CO_2 (PCT)	SO_2 (PPM)	HC (PPM)
133	0.	5.05	542.	0.	1256.	0.	10.	15.05	0.	3.
134	0.	2.47	396.	0.	390.	0.	181.	15.83	0.	3.
135	0.	4.88	747.	736.	262.	0.	10.	14.89	0.	11.
136	0.	3.74	520.	511.	502.	0.	25.	15.20	0.	10.
137	0.	2.71	832.	818.	790.	0.	17.	15.19	0.	6.
150	0.	5.54	883.	879.	1421.	0.	23.	15.36	0.	32.
151	0.	3.08	508.	502.	490.	0.	713.	13.48	0.	11.
152	0.	5.50	848.	840.	733.	0.	434.	14.52	0.	5.
153	0.	1.94	456.	456.	449.	0.	370.	15.07	0.	0.
200	0.	2.02	558.	556.	569.	0.	20.	15.65	0.	0.
201	429.	2.22	939.	927.	899.	0.	204.	15.13	0.	0.
202	431.	3.27	1146.	1137.	1114.	0.	17.	15.64	0.	0.
203	417.	3.31	548.	536.	1766.	6.	240.	15.13	0.	0.
023	415.	2.83	495.	490.	540.	3.	567.	15.89	0.	0.
204 A	0.	1.32	586.	574.	552.	0.	160.	14.97	2610.	5.
205	437.	2.27	553.	543.	626.	11.	0.	14.35	0.	0.
206	432.	3.32	641.	632.	657.	8.	0.	15.84	0.	0.

NOT REPRODUCIBLE

Appendix C

Sample Data Tables (Both Raw and Reduced)
(Example Includes Selected Data From Test #129)

This appendix presents examples of typical raw data on boiler operating conditions and emission monitor results for selected tests. A typical computer analysis of a test is also shown here.

The following pages are exemplary of the data that has been recorded during the test. It was impractical to include here, the great volume of data recorded. However, additional raw data is available to the reader as part of a "Data Supplement" published under this contract.

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CONTROL ROOM BOARD OPERATING DATA
GULF POWER COMPANY CRIST GENERATING STATION UNIT NO. 7

ITEM	UNITS	START	FINISH	START	FINISH	START	FINISH	START	FINISH
Run No.	-	129		130		131		132	
Date of Run		2-8-78		2-9-78		2-15-78		2-16-78	2-17-78
Time		10:12	10:42	11:26 PM	11:53 PM	2:37	3:00	10:47 PM	1:20 AM
Cold Reheat	PSIG			395	379	373	369	360	360
Hot Reheat	PSIG			759	741	735	732	723	374
Cold Reheat	°F			645	650	608	684	609	611
Prim. Air Out "A"	°F	325	325	270	266	335	331	298	285
Prim. Gas Out "A"	°F	190	190	156	156	198	196	177	175
Prim. Air Out "B"	°F	315	385	362	293	370	376	318	308
Prim. Gas Out "B"	°F	235	235	178	175	240	233	202	200
Sec. Air In "A"	°F	60	60	65	66	74	74	71	67
Gas Out "A"	°F	235	285	279	277	255	255	280	271
Sec. Air In "B"	°F	60	60	66	66	78	76	69	66
Gas Out "B"	°F	370	370	333	331	329	327	298	294
FD "A" Disch. Pres.	In H_2O	19	19	8	8	9	9	6	6
FD "B" Disch. Pres.	In H_2O	20	20	8	8	9	9	7	7
Sec. Air Htr 7A - Gas Dif.	In H_2O	7.6	7.5	3.2	2.2	3.3	3.2	3	3
Sec. Air Htr 7B - Gas Dif.	In H_2O	6.8	7.0	3.2	3.5	3.7	3.6	3	3
Furnace Gas Pres.	In H_2O	-1	-1	-1	-1	-1	-1	-1.2	-1
Econ. Inlet Gas	In H_2O	-4.5	-5	-2	-2	-2	-2.5	-2	-2
Pulv. A - Coal Feed	RP/H	50	50	-0	-0	0	0	0	0
Pulv. B - Coal Feed	RP/H	75	75	-0	-0	57	57	53	53
Pulv. C - Coal Feed	RP/H	81	81	74	74	57	57	58	59
Pulv. D - Coal Feed	RP/H	74	76	74	74	56	57	57	58
Pulv. E - Coal Feed	RP/H	64	63	72	70	55	56	57	57
Pulv. F - Coal Feed	RP/H	72	74	64	64	58	56	59	59
Gross Load	MW	460	445	330	319	300	300	298	298
Throttle Pres.	PSIG	2175	2125	2100	2025	1875	1925	2000	1975
Spray - RH $x10^5$	PPH	(NOT WORKING)							
Spray - Lower SH	PPH	85	25	185	180	130	110	125	110
Spray - Upper SH	PPH	(NOT WORKING)							
Reheat Steam Flow	PPH								
Main Steam Flow	PPH			2.8					
Feed Water Flow	PPH			2.0					

65358

TEST NO.		129		130		131		132	
ITEM	UNITS	START	FINISH	START	FINISH	START	FINISH	START	FINISH
S. H. Out Steam	°F	975	1013	1010	1018	969	975	986	985
R.H. Out Steam	°F	1000	1013	990	947	944	935	954	955
Sec. Air Out "A"	°F	617	623	600	598	565	560	585	580
Sec. Air Out "B"	°F	612	620	595	593	580	573	551	548
Gas Out "B" (ECONOMSR)	°F	750	757	700	700	675	670	670	663
Gas Out "A" (ECONOMSR)	°F	760	758	610	608	670	670	663	660
Avg. Pulv. Temp.	°F	135	140	130	125	140	140	135	140
% O_2 - "B"	%	2.98	3.0	3.1	3.05	4.2	4.35	3.1	3.0
% O_2 - "A"	%	7.72	7.58	6.2	5.5	7.8	7.85	6.35	6.4
Main Steam Flow	MP/H	3.9	3.9	2.8	2.6	2.6	2.7	2.6	2.5
Feed Water Flow	MP/H	3.45	3.1	2.0	1.9	2.0	2.0	1.96	1.95
R. H. Steam Flow	MP/H					(NOT WORKING)			
Condensate Flow	MP/H	2.5	2.4	1.8	1.7	1.6	1.45	1.55	1.5
Lower S. H. Spray									
Upper S. H. Spray									
R. H. Spray									
Oil Flow	MP/H	4.6	4.6	3.1	3.2	3.5	3.5	3.2	3.2
Flame Opacity									

Oper. Conditions:				
Excess Air	(Normal) HIGH	HIGH	NORM	NORM
Firing Pattern	S1	A&B MILL OFF S18	S19 (A OFF)	S19 (A OFF)
Sec. Air Reg.	60-40-40	60-40-40	60-40-40	60-40-40
Gross Load	440-460	Low (325)	Low	Low
Pulv. - Air Only	NONE	A&B	A	A
Notes:	Coal Samples Taken	Coal Samples Taken Begin Gas Taps	Brought Load Up And Down During This Test	Gas Taps And SO_2
			SO_2 & SO_3 (See Notes)	

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80 COLUMN DATA SHEET

PROGRAM SO_2/SO_3 TEST @ ABOUT 450MW (WET CHEMISTRY SAMPLE TAKEN OFF OF MIDDLE PROBE ON BOX NO. 4.) EHM.

C	TEST #	LTR	DATE	START TIME	STATION IDENTIFICATION	UNIT	DUCT PRESSURE	START W.BULB	START D.BULB	FINISH W.BULB	FINISH D.BULB	DUCT LEVELS	ATMOS PRESSURE
	129		80208		CRIST GULF POWER	7							

LINE	TIME	PROBE NO.	TEMP	O2	CO			NOX	CHEMI NO	HC	NDIR NO		NDIR NO2	CO2		SO2	(PSIG) SAMPLE PRESSURE
1	1022	1		7.5	4	L	2	690.		2.	45.	1		62.	1		
2	1023	2		5.7	10	L	2	825.		1.	52.	1		69.	1		
3	1024	3		5.1		L	2	850.		8.	53.	1		72.	1		
4	1026	4		4.9		L	2	820.		2.	52.	1		72.	1		
5	1027	1		7.4		L	2	700.		3.	45.	1		62.	1		
6	1028	2		5.6		L	2	815.		1.	52.	1		68.	1		
7	1030	3		5.0		L	2	840.		5.	52.	1		71.	1		
8	1032	4		4.8		L	2	820.		1.	52.	1		71.	1		
9	1034	1		7.2		L	2	720.		2.	45.	1		61.	1		
10	1036	2		5.6		L	2	850.		1.	53.	1		69.	1		
11	1037	3		5.0		L	2	835.		3.	53.	1		71.	1		
12	1039	4		4.9		L	2	830.		1.	53.	1		73.	1		
13																	
14																	
15																	
16																	
17																	
18																	
19																	
20																	

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STATION- CRIST GULF POWER
UNIT NO.- 7
DATE- 2/ 8/76
TEST NO.- 129

AS MEASURED

PROBE	TEMP. (C)	O2 (PCT)	NOX (CHEMI) (PPM)	NO (CHEMI) (PPM)	NO (NDIR) (PPM)	NO2 (PPM)	CO (PPM)	CO2 (PCT)	SO2 (PPM)	HC (PPM)
1	0.	7.50	690.	0.	718.	0.	8.	10.24	0.	2.
2	0.	5.70	825.	0.	848.	0.	20.	11.79	0.	1.
3	0.	5.10	850.	0.	868.	0.	0.	12.49	0.	8.
4	0.	4.90	820.	0.	848.	0.	0.	12.49	0.	2.
1	0.	7.40	700.	0.	718.	0.	0.	10.24	0.	3.
2	0.	5.60	825.	0.	848.	0.	0.	11.56	0.	1.
3	0.	5.00	840.	0.	848.	0.	0.	12.26	0.	5.
4	0.	4.80	820.	0.	848.	0.	0.	12.26	0.	1.
1	0.	7.20	720.	0.	718.	0.	0.	10.03	0.	2.
2	0.	5.60	850.	0.	868.	0.	0.	11.79	0.	1.
3	0.	5.00	835.	0.	868.	0.	0.	12.26	0.	3.
4	0.	4.90	830.	0.	868.	0.	0.	12.73	0.	1.

STATION- CRIST GULF POWER
UNIT NO.- 7
DATE- 2/ 8/76
TEST NO.- 129

CORRECTED TO 3 PER CENT O2

PROBE	TEMP. (C)	O2 (PCT) (MEAS)	NOX (CHEMI) (PPM)	NO (CHEMI) (PPM)	NO (NDIR) (PPM)	NO2 (PPM)	CO (PPM)	CO2 (PCT)	SO2 (PPM)	HC (PPM)
1	0.	7.50	920.	0.	957.	0.	11.	13.66	0.	3.
2	0.	5.70	971.	0.	998.	0.	24.	13.87	0.	1.
3	0.	5.10	962.	0.	982.	0.	0.	14.14	0.	9.
4	0.	4.90	917.	0.	949.	0.	0.	13.96	0.	2.
1	0.	7.40	926.	0.	950.	0.	0.	13.56	0.	4.
2	0.	5.60	964.	0.	992.	0.	0.	13.52	0.	1.
3	0.	5.00	945.	0.	954.	0.	0.	13.79	0.	6.
4	0.	4.80	911.	0.	943.	0.	0.	13.62	0.	1.
1	0.	7.20	939.	0.	936.	0.	0.	13.08	0.	3.
2	0.	5.60	994.	0.	1014.	0.	0.	13.78	0.	1.
3	0.	5.00	939.	0.	976.	0.	0.	13.79	0.	3.
4	0.	4.90	928.	0.	970.	0.	0.	14.23	0.	1.
AVG.										
1	0.	7.37	929.	0.	948.	0.	11.	13.43	0.	3.
2	0.	5.63	976.	0.	1001.	0.	24.	13.72	0.	1.
3	0.	5.03	949.	0.	971.	0.	0.	13.91	0.	6.
4	0.	4.87	919.	0.	954.	0.	0.	13.94	0.	1.
1+2	0.	6.50	952.	0.	975.	0.	17.	13.58	0.	2.
3+4	0.	4.95	934.	0.	962.	0.	0.	13.92	0.	4.
1,2,3,+4	0.	5.72	943.	0.	968.	0.	17.	13.75	0.	3.

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APPENDIX D

CONVERSION FACTORS

English and Metric Units to SI Units

To Obtain	From	Multiply By
ng/J	lb/MBtu	430
ng/J	g/MCal	239
GJ hr^{-1} m^{-2}	MBH**/ft^2	11.356
GJ hr^{-1} m^{-3}	MBH/ft^3	37.257
GJ/hr	10^3 lb/hr* or MBH	1.055
MW	10^3 lb/hr* or MBH	0.293
m	ft	0.3048
cm	in	2.54
cm	mils	0.00254
m^2	ft^2	0.0929
m^3	ft^3	0.02832
Kg	lb	0.4536
°Kelvin	°Rankin	5/9
°Celsius	°Fahrenheit	$t_c = (5/9)(t_F-32)$
°Kelvin	°Fahrenheit	$t_k = ((5/9)(t_F-32)) + 273$
°Kelvin	°Celsius	$t_k = t_c + 273$
Pa	psig	$P_{pa} = (P_{psig} + 14.7)(6895)$
Pa	psia	$P_{pa} = (P_{psia})(6895)$
Pa	iwg*** (39.2°F)	$P_{pa} = (P_{iwg})(249.1)$
Pa	in Hg	3385
in H_2O	in Hg	13.6
atm	in Hg	1/760
mmHg	in Hg	25.4
psi	in Hg	0.491

To Obtain ng/J for	Multiply Concentrations (in ppm dry at 3% O_2) by
Natural Gas Fuel	
CO	0.310
HC	0.177
NO_x, NO, or NO_2 (As Equivalent NO_2)	0.510
SO_x (SO_2)	0.709
Oil Fuel	
CO	0.341
HC	0.195
NO_x, NO, or NO_2 (As Equivalent NO_2)	0.561
SO_x (SO_2)	0.780
Coal Fuel	
CO	0.372
HC	0.213
NO	0.395
NO_x, NO, or NO_2 (As Equivalent NO_2)	0.589
SO_x (SO_2)	0.850

---

*lb/hr of equivalent saturated steam. (For water, the heat of the liquid-gas phase change is about 10^3 Btu/pound.)

**10^6 Btu/hr

***The symbols iwg and in H_2O g are used interchangeably in this report to indicate guage pressure in inches of water.

a5358

APPENDIX D (CONTINUED)

CONVERSION FACTORS

SI Units to Metric or English Units

To Obtain	From	Multiply By
g/Mcal	ng/J	0.004186
10^6 Btu	GJ	0.948
MBH/ft^2	GJ·$hr^{-1}m^{-2}$	0.08806
MBH**/ft^3	GJ·hr^{-1}·m^{-3}	0.02684
Btu	gm cal	3.9685×10^{-3}
10^3 lb/hr* or MBH	GJ/hr	0.948
10^3 lb/hr* or MBH	MW	3.413
lb/MBtu	ng/J	0.00233
ft	m	3.281
in	cm	0.3937
mils	cm	393.7
ft^2	m^2	10.764
ft^3	m^3	35.314
lb	Kg	2.205
°Rankin	°Kelvin	1.80
°Fahrenheit	°Celsius	$t_F = 9/5(t_c)+32$
°Fahrenheit	°Kelvin	$t_F = 1.8\ T_k - 460$
°Rankin	°Fahrenheit	$t_R = t_F + 460$
psig	Pa	$P_{psig} = (P_{pa})(0.0001450)-14.7$
psia	Pa	$P_{psia} = (P_{pa})(0.0001450)$
iwg*** (39.2°F)	Pa	$P_{iwg} = (P_{pa})(0.004014)$
in Hg	Pa	0.000295
in Hg	in H_2O	1/13.6
in Hg	atm	760
in Hg	mm Hg	1/25.4
in Hg	psi	2.036

To Obtain ppm (dry) at 3% O_2 for	Multiply Flow Concentrations in ng/J, by
Natural Gas Fuel	
CO	3.23
HC	5.65
NO_x, NO, or NO_2 (As Equivalent NO_2)	1.96
SO_x (SO_2)	1.41
Oil Fuel	
CO	2.93
HC	5.13
NO_x, NO, or NO_2 (As Equivalent NO_2)	1.78
SO_x (SO_2)	1.28
Coal Fuel	
CO	2.69
HC	4.69
NO	2.52
NO_x, NO, or NO_2 (As Equivalent NO_2)	1.71
SO_x (SO_2)	1.18

---

*lb/hr of equivalent saturated steam. (For water, the heat of the liquid-gas phase change is about 10^3 Btu/pound.)

**10^6 Btu/hr

***The symbols iwg and in H_2O g are used interchangeably in this report to indicate guage pressure in inches of water.

APPENDIX E

ANALYTICAL PROCEDURES
FOR
SASS TRAIN SAMPLES (17)

Sample Preparation And Analysis

A sample preparation and analysis procedure scheme as shown in Figure E-1 was devised to analyze particulates (by size), condensates, XAD-2 porous polymer resins and impinger solutions for metals, PNA's, ard anions.

Sample preparation for the cyclone catches is shown in Figure E-1. The washes from the cyclones were evaporated to dryness and weighed. The mass of material collected by each cyclone and associated washings are detailed in Table E-1. The dried solid material from the rinses were combined with the appropriate cyclone catches. Portions of the sample were then analyzed for metals and fluoride. Another portion was then analyzed for PNA's and chlorinated organics. The solids from each of the three cyclone catches were extracted for water soluble sulfates and nitrates.

Sample preparation of the condensate samples is illustrated in Figure E-1. The aqueous XAD-2 resin rinses along with the container washings were added to the condensate sample. Analyses were then performed on this sample to determine the metal and anion content.

Preparation and analysis procedures for PNA's and metals on the XAD-2 porous polymer resin and impinger solutions are also shown on Figure E-1. Details of the analytical procedures and amendments to the Level 1 methodology are delineated in the following:

Cleaning Procedures

1. All sample containers and lab glassware are:
    a. Visually inspected
    b. Washed with hot detergent water
    c. Rinsed thoroughly with deionized (DI) water.
2. Further treatment depends on the future use of the glassware.

Organic Cleanup

1. Follow cleaning procedure with the following additions.
2. Soak in chromic acid for 30 minutes.

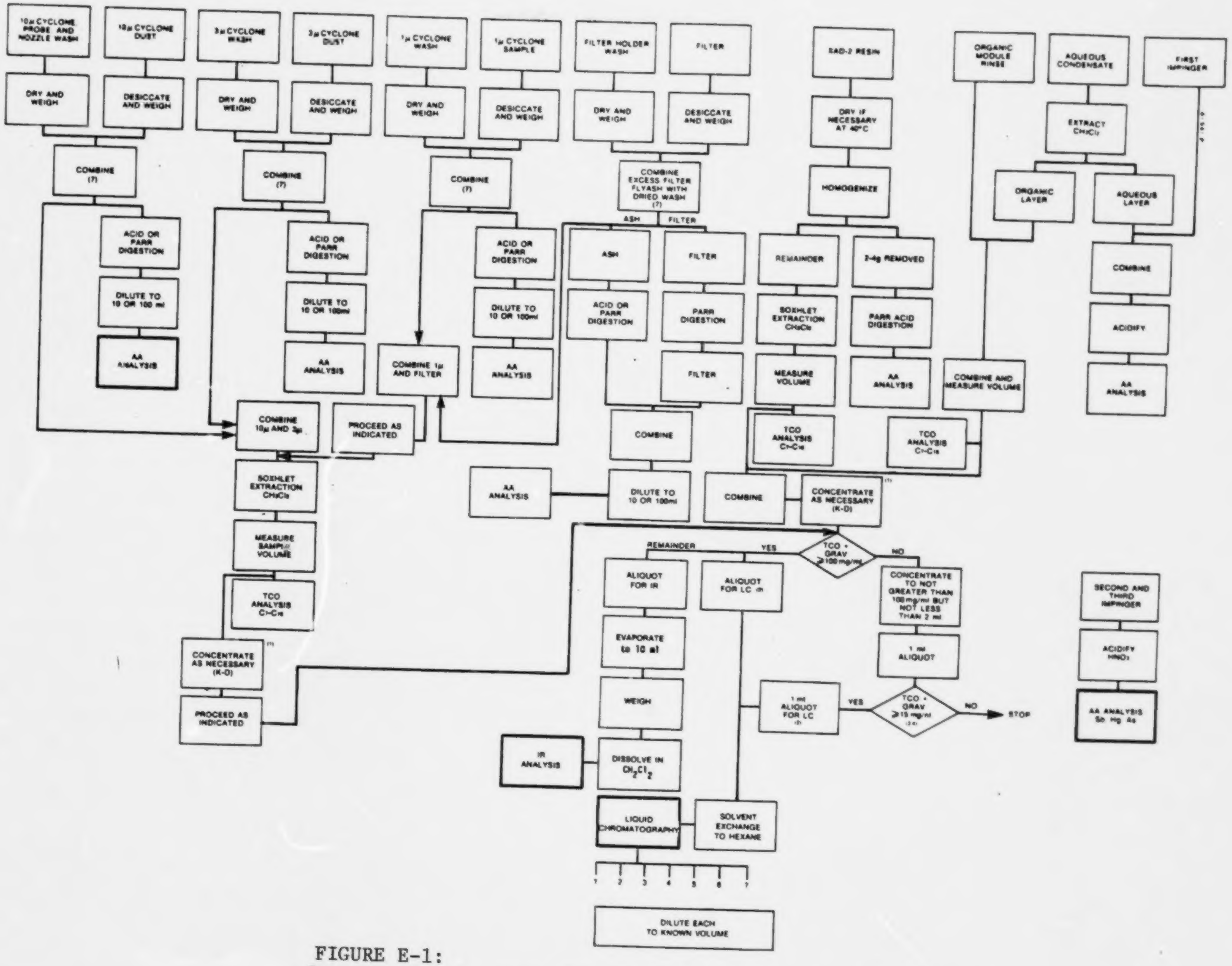
10μ CYCLONE PROBE AND NOZZLE WASH
10μ CYCLONE DUST
3μ CYCLONE WASH
3μ CYCLONE DUST
1μ CYCLONE WASH
1μ CYCLONE SAMPLE
FILTER HOLDER WASH
FILTER
XAD-2 RESIN
ORGANIC MODULE RINSE
AQUEOUS CONDENSATE
FIRST IMPINGER
DRY AND WEIGH
DESICCATE AND WEIGH
DRY IF NECESSARY AT 40°C
EXTRACT CH2Cl2
COMBINE (7)
COMBINE EXCESS FILTER FLYASH WITH DRIED WASH (7)
ASH
FILTER
HOMOGENIZE
ORGANIC LAYER
AQUEOUS LAYER
ACID OR PARR DIGESTION
DILUTE TO 10 OR 100 ml
AA ANALYSIS
PARR DIGESTION
REMAINDER
2-4g REMOVED
SOXHLET EXTRACTION CH2Cl2
PARR ACID DIGESTION
MEASURE VOLUME
COMBINE AND MEASURE VOLUME
ACIDIFY
COMBINE 1μ AND FILTER
COMBINE 10μ AND 3μ
PROCEED AS INDICATED
COMBINE
TCO ANALYSIS C7-C16
MEASURE SAMPLE VOLUME
CONCENTRATE AS NECESSARY (K-D) (1)
TCO + GRAV ≥100 mg/ml
YES
NO
REMAINDER
ALIQUOT FOR IR
ALIQUOT FOR LC (2)
CONCENTRATE TO NOT GREATER THAN 100 mg/ml BUT NOT LESS THAN 2 ml
1 ml ALIQUOT
1 ml ALIQUOT FOR LC (2)
TCO + GRAV ≥15 mg/ml (3,4)
STOP
EVAPORATE to 10 ml
WEIGH
IR ANALYSIS
DISSOLVE IN CH2Cl2
LIQUID CHROMATOGRAPHY
SOLVENT EXCHANGE TO HEXANE
1 2 3 4 5 6 7
DILUTE EACH TO KNOWN VOLUME
SECOND AND THIRD IMPINGER
ACIDIFY HNO3
AA ANALYSIS Sb Hg As

FIGURE E-1:
Sample analysis procedures for SASS cyclones, and organic module samples.

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TABLE E-1

MASS OF MATERIAL COLLECTED IN CYCLONES
(Reported in Grams)

GULF POWER COMPANY
CRIST STATION, NO. 7 BOILER

	Test No. 3 SASS 6/22/78	Test No. 4 SASS 6/23/78
10 μm Cyclone & Probe	10.78093	48.20833
10 μm Wash	1.64931	0.39421
10 μm Total	12.43024	48.60254
3 μm Cyclone	16.89219	35.58187
3 μm Wash	0.48543	0.43547
3 μm Total	17.37762	36.01734
1 μm Cyclone	5.38432	12.70445
1 μm Wash	0.14361	0.55059
1 μm Total	5.52793	13.25504
Filter	1.53143	2.79013
Filter Housing Wash	0.15808	0.11090
Filter Total	1.68951	2.90103

3. Rinse thoroughly with DI water.
4. Shake off excess water.
5. Rinse with acetone or methanol. Dry.
6. Cap with muffled Aluminum foil and store in cabinets.
7. Rinse with solvent of the analysis directly before use.
8. When washing bottles, caps should be lined with teflon liners and cleaned with solvents also.
9. Certain glassware (K-D's, ampules, Synder columns, sulfur tubes) should be muffled for 4 hours at 450°C at the end of a day's use. Muffling instructions are given by the analyst.
10. Glassware to be stored for any period of time outside the laboratory are placed in sealed containers that are marked with cleaning date, dishwasher's initials, and a synopsis of the cleaning method.

Inorganic Cleanup

1. Follow cleaning procedure with these additions.
2. Soak in 1:1 HNO_3 for two hours.
3. Rinse with DI water thoroughly.
4. Drain. Dry.

Liquid Chromatography Separation

1. This technique separates organic mixtures into functional groups (classes).
2. Column: 200 mm x 10.5 mm glass with Teflon stopcock and solvent reservoir. Clean column using organic clean-up procedure. Packing: Merck Silica Gel, 60 to 200 mesh. Activate silica gel at 110°C for 2 hours before use.
3. Place a small plug of pre-extracted glass wool at the bottom of the column and tap down with rinsed store rod. Weigh approximately 6 grams activated silica gel. Transfer in a slurry to column. Vibrate column briefly to settle silica gel. Pour hexane through the silica gel until all bubbles and cracks are eliminated. Leave a small amount of hexane covering the top of the silica gel bed until the sample is placed on the column. If cracks and bubbles remain wrap an acetone wetted wipe around the column of the imperfections. Periodically wet wipe with acetone while running hexane through the column.

4. Samples must go through solvent exchange if they have $\geq$ 2 mg TCO per original sample before they are placed on the column. Take an aliquot containing approximately 15-100 mg organic material and add to 200 mg activated silica gel in a clean 50 ml beaker. Reduce solvent volume to 1 ml, no less, using a stream of clean nitrogen. Warm sample manually or in a 40°C water bath during evaporation to prevent condensation of atmospheric moisture into the sample. Add 1 ml cyclopentane. Reduce volume as above to 1 ml. Repeat for a total of three solvent exchanges.

5. Allow hexane on the column to elute until level with the top of the silica gel. Place cyclopentane-silica gel slurry onto the top of the column with a Pasteur pipette. Gently run the sample down the side of the column to avoid disturbing the silica gel bed during sample placement.

6. Add solvent slowly down the sides of the column. The solvent series, from least polar to most polar, is as follows:

Fraction	Solvent	Volume (mls)	Compound Type Eluted
1	Hexane	25	Aliphatic hydrocarbons
2	20% methylene chloride in Hexane	10	Aromatic HC's, POM, PCB Halides
3	50% methylene chloride in Hexane	10	Esters, Ethers, Epoxides, Nitro Compounds
4	Methylene chloride	10	Phenols, Esters, Ketones, Aldehydes, Phthalates
5	5% methanol in Methylene chloride	10	Phenols, Alcohols, Phthalates, Amines
6	20% methanol in methylene chloride	10	Amines, Sulfonates, Aliphatic Acids, Carboxylic Acid Salts
7	50% methanol in methylene chloride	10	Sulfonates, Sulfoxides, Sulfonic Acids

Rinse solvent exchange vessel with part of solvent 1 and add to column. Repeat with solvents 2, 3, 4. For each fraction, collect the same volume of solvent that was added. Fractions are kept in amber glass bottles prepared by organic cleanup procedure. Make certain that the caps include Teflon liners. Label bottles and mark solvent level on bottle with indelible ink. Refrigerate.

7. A blank solution comparable to each sample type must be separated by LC. Fractions are collected and analyzed as samples.

Liquid Chromatography on SASS Samples

1. Follow liquid chromatography separation method with the following variations.

2. Samples must meet Level 1 criteria of $\geq$ 15 mg/ml TCO + GRAV to undergo LC separation.

3. Samples with low TCO ($\leq$ 2 mg) may use a modified solvent exchange system. Add aliquot containing 15-100 mg material to a small amount of activated silica gel. Evaporate the solvent. Load the sample + the silica gel directly onto the column.

4. Neat organic liquids: weight the aliquot containing approximately 100 mg of organic material into a tared glass weighing funnel. Add 200 mg activated silica gel. Mix. Transfer to column.

5. Each LC fraction is analyzed by TCO (mg), GRAV (mg), and IR. Those passing Level 1 criteria for mass loading are further analyzed by LRMS or GC/MS. Criteria are:

   Fractions 1, 4, 5, 6, 7: If GRAV is $\geq$ 0.5 mg $(f)/m^3$ for XAD-2 resin, or $\geq$ 1 mg (f)/Kg for ash samples, then these fractions are analyzed by LRMS.

   Fractions 2,3: If GRAV is $\geq$ 0.5 mg$(f)/m^3$ for XAD-2, or $\geq$ 1 mg (f)/kg for ash samples, then these samples are analyzed by GC/MS. (f is factor used to correct aliquot value to total sample value).

Total Chomatographable Organics (TCO)

1. TCO must be performed on extracts and solutions prior to *any* concentration step. Several TCO's may be run on one sample at successive steps in the analytical scheme and such steps must be shown on label.

2. GC Parameters
   Detector: FID
   Column: 6 ft x 1/8 in glass 10% OV-17 or OV-101 on 100/120 mesh

   Column Temperature Program:

   40°C 2 min
   10°C/min
   250°C max - hold 5 minutes or until chromatogram returns to baseline

   Injection Temp: 250°C
   Detector Temp: 280°C

Column Flow: 35 ml/min Helium
Flame Gases: 22.5 ml/min Hydrogen
30 ml/min Air
Sample Size: 2-2.5 μl

3. Standard mixtures of C_6 -C_{18} aliphatic hydrocarbons are injected daily to check response factors and instrumental performance. Integration of peaks should be set to begin before C_7 and end after C_{17}.

Blanks for samples should be run, including blanks for all 7 LC fractions. Area counts from blanks are subtracted from sample area counts.

$$\text{Response Factor (RF)} = \text{ng}/\mu\text{l}/\text{area count}$$

$$\text{mg TCO} = \frac{(\text{Area counts of sample} - \text{blank counts})(\text{avg RF})(\text{total volume } \mu\text{l})}{10^6}$$

Gravimetric Analysis (GRAV)

I. Organic Liquids

A. Wash Al weighing dish with the appropriate solvent. Dry in desiccator 3 hours. (Alternatively, muffle dishes at 200°C if sample requires further organic analysis). Use solvent washed latex gloves to handle dishes from this point on. Tare to 0.01 mg.

B. Transfer material to dish. Evaporate solvent. Re-dry dish in desiccator 3 hours or more to constant weight ($\pm$0.1 mg). Weigh to 0.01 mg.

II. Solid Samples

A. Wash Al weighing dish with appropriate solvent. Dry in desiccator 3 hours. Tare to 0.01 mg.

B. Transfer samples quantitatively to Al dishes. Brush small particles into dish using teflon policeman. Dry 24 hours in desiccator. Weigh to 0.01 mg. Place in desiccator for another 6 hrs. Reweigh. The difference between weighings should not exceed 0.5 mg. Samples should not be exposed to laboratory air longer than 2 minutes.

C. Return samples to their original containers.

GRAV on Sass Organic Extracts

1. Follow Gravimetric Analysis method with the following modifications.
2. Wash pipette with methylene chloride. Dry. Use no more than 5 ml of extract or 1/2 total sample whichever is smaller. Pipette extract volume into Al dish.
3. Evaporate solvent under a gentle stream of clean nitrogen.
4. Add approximately 1 ml methylene chloride to Al dish after last weight is taken. Transfer quantitatively to a clean glass vial. Label with sample ID, lab number, words GRAV-IR, and date. Refrigerate.
5. GRAV values are reported as mg/ml.

GRAV on Solvent Wash Samples

1. Use gravimetric analysis method with the following modifications.
2. Wash solutions are added to Al dish in successive increments if volume is greater than 10 mls. Swirl solvent to transfer all particulates with it into weighing dish, and then add a small amount of solvent to container as a rinse.
3. Very low heat may be added to hasten evaporation unless organic analysis on the wash dust follows.
4. After the last weighting, add dust from the weighing dishes to the corresponding dust container.

GRAV on Filters and Filter Dust

1. Use gravimetric analysis method with the following modifications.
2. Filters should be placed in the desiccator resting in the large half of their petri plate container. Filters should be placed directly on balance for weighing with stainless steel tweezers. All loose dust and/or filter scraps must be weighed with the filter. Repeat to a constant weight of ±0.5 mg.

SASS Organic Module Rinse-XAD-2 Condensate

1. Extract three times with methylene chloride at ratio condensate: methylene chloride 30:1. If there is a significant amount of methylene chloride in the sample from the rinse, use this as first extraction volume (minimum of 30 ml methylene chloride used per extract).

2. Combine all organic portions, measure, and record volume. Remove 1 ml for TCO into methylene chloride rinsed glass vial, label, mark solvent level and refrigerate at 5°C.

3. Add aqueous portion to first impinger for elemental analysis. Measure and record total volume.

4. Make blanks similarly by using a comparable amount of the water blank from the test.

5. Add organic extract to the XAD-2 organic extract. Concentrate the combined extracts. Proceed with Level 1.

Soxhlet Extraction and Concentration of Solid Samples

I. Extraction

1. Dry sample in desiccator or at low heat to constant-weight.
2. Clean Soxhlet apparatus by organic cleanup procedure. This includes round-bottom (R-B) receiving flask, thimble and Soxhlet extractor. Rinse the inside of the condenser with the appropriate solvent.
3. Use solvent rinsed latex gloves whenever handling any clean glassware that will contact the sample and/or solvent. Be especially careful with the thimble.
4. Weigh the thimble. Small thimbles are weighed to 0.01 mg. Large thimbles are weighed to 1.0 g. Add dry sample. Reweigh. Cover sample with pre-extracted glass wool plug.
5. Assemble Soxhlet apparatus:
    a. Place R-B flask in heating mantle. Add 10-15 muffled glass beads.
    b. Carefully lower the thimble into the Soxhlet extractor.
    c. Connect R-B flask and extractor. Do not use grease in joints.
    d. Add 2-3 x extractor flushing volume of solvent.
    e. Connect condenser. Cover top with Al foil. Turn on cooling water, with flow in on bottom.
    f. Plug mantles into rheostat. Turn on to proper setting.

6. Extract sample 24 hour. Check solvent level periodically. Cool. Remove condenser.

7. Remove thimble from extractor with long tongs. Disconnect extractor from round-bottom flask. Pour any solvent remaining in it into R-B flask. Rinse extractor with solvent and add to R-B flask.

8. Measure volume of extract in a clean graduated cylinder. Record volume.

II. Concentration

1. Clean a Kuderna-Danish (K-D) concentrator, ampule, Synder column, and sulfur tube.

2. Assemble K-D and ampule. Put 1 glassbead (muffled) in ampule. Place 1 inch of muffled Na_2SO_4 in sulfur tube. Pass sample through Na_2SO_4 into the K-D. Rinse with solvent after the extract has passed through completely and collect washes in the K-D.

3. Add Synder column to K-D. Moisten with a small amount of solvent.

4. Reduce solvent volume on a steam bath. DO NOT allow sample to go to dryness. Stop concentration if sample begins to precipitate.

5. Cool. Remove Synder column and K-D carefully. Rinse the sides of the ampule with the extract using a muffler Pasteur pipette. Transfer extract with Pasteur pipette to a muffled glass vial or bottle. Add rinse to the extract in the vial. Repeat two more times if possible, recording total volume of solution including rinses.

6. Bring extract to proper volume. Mark solvent level with indelible ink. Label. Refrigerate.

SASS Samples Soxhlet Extraction

Use soxhlet extraction method with the following additions:

1. Solvent is methylene chloride.

2. Run blank portions or methylene chloride through extractor procedure as a system blank.

3. Sample sizes

A. Fly Ash and Filters

Combine portions of the dry 10 μm and 3 μm fly ash (or 1 μm fly ash and filter dust) in proportion to total mass collected. If the weight is $\leq$ 10 grams, use all for organic analysis. If weight is $\geq$ 10 grams, use a 10-20 gram portion. The R-B flask may be 250 or 50 ml.

B. XAD-2 Resin

Dry at low heat till all solvent is evaporated. Weigh. Remove aliquot for AA (approx. 2 g). Transfer the entire sample to large Soxhlet thimble. Traces in resin container are washed into the thimble with $MeCl_2$ after it is placed in the extractor. All wash solvent must be caught in the extractor. Use a 3-liter R-B receiving flask.

C. Bottom Ash

Weight 250-300 g dry and ground bottom ash into large thimble. Use 3000-ml R-B receiving flask.

D. Electrostatic Precipitator Ash; Mechanical Hopper Ash

Weigh 20-25 g into medium thimble. Use a 500-ml R-B receiving flask.

4. Remove 1 ml of extract for TCO before any concentration step. Use a solvent rinsed volumetric pipette. Mark the level of the solvent on the vial with indelible ink. Label, refrigerate.

5. Samples will generate at least 2 TCO´s, one straight from the Soxhlet extract, one after the extract is concentrated. If concentration is done in steps, more TCO´s/per samples will be done. TCO values provide a guideline for the degree of concentration of the extract. The maximum concentration is 10 mg/ml. The minimum volume is 2 ml. Concentration should always be stopped if a precipitate forms.

Mass Spectrometry Analysis

1. Introduction

Tests 3 and 4 were analyzed by Acurex using Level 1 environmental assessment methodology with additional GCMS analysis of selected samples. The Test 4 inlet XAD-2 sample did not meet the criteria for liquid chromatographic (LC) separation. This unseparated sample was analyzed by GCMS. The Test 3 inlet XAD-2 sample was subjected to LC fraction. The combined LC fractions 2 and 3 were analyzed on GCMS.

LC fractions which met the Level 1 criteria of ≥ 0.5 ng/m^3 were analyzed by low resolution mass spectrometry. These include LC fraction 1, combined LC fractions 4 and 5, and combined LC fractions 6 and 7.

2. Methods

GCMS and LRMS analyses were conducted using a Finnegan Corporation Model 4000 computerized combined gas chromatograph/mass spectrometer. LRMS analyses were initiated by evaporating a 10-microliter sample in a glass capillary and inserting the capillary into the source region of the mass spectrometer using the solid probe inlet of the instrument. The filament of the mass spectrometer was turned on and the mass range of 45 to 475 a.m.u. was scanned continuously while the initially cold probe (0°C) was slowly heated to 250°C.

GCMS experiment were conducted on a six foot, 1/4 inch O.D. column of 1 percent SP 2250 on 100/120 mesh Supelcoport interfaced via an all-glass jet separator to the mass spectrometer. Two microliter samples were injected onto the column at 60°C and the column was temperature programmed to 265°C at 8°C per minute. After an initial 1.5 minutes, the mass range 45 to 475 a.m.u. was continuously scanned at 2.0 second intervals.

Prior to initiation of data collection, the mass spectrometer was tuned against the calibration compound decafluorotriphenylphosphine (DFTPP). To assure sensitivity for polycyclic aromatics a standard mixture containing 40 mg of each species asterisked in Table E-2 was analyzed. This standard run also provided response factors which were used to calculate the quantitative data. The raw mass spectral data was screened for the compounds listed in Table E-2.

3. Calculations

Samples are spiked with the quantitation standard at the level of twenty micrograms d_{10} - anthracene per millimeter of sample. The amount of a particular compound in the sample is calculated using its response factor relative to d_{10} - anthracene. This value is corrected for dilution factors and for method blank contributions. Finally, sample compound values are adjusted to reflect stack emissions (XAD-2 extracts).

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TABLE E-2

COMPOUNDS SOUGHT IN PENSACOLA, FLORIDA ... ORGANIC SAMPLES

- * 4-bromophenyl phynyl ether
- * bis (2-chloroisopropyl) ether
- * bis (2-chloroethoxy) methane
- * hexachlorobutadiene
- * hexachlorocyclopentadiene
- * isophorone
- * naphthalene
- * nitrobenzene
- * N-nitrosodiphenylamine
- * N-nitrosodi-n-propylamine
- * bis (2-ethylhexyl) phthalate
- * butyl benzyl phthalate
- * di-n-buyl phthalate
- * di-n-octyl phthalate
- * diethyl phthalate
- * dimethyl phthalate
- * benzo(a)anthracene
- * benzo(a)pyrene
- * 3,4-benzofluoranthene
- * benzo(k)fluoranthene
- * chrysene
- * acenaphthylene
- * anthracene
- * benzo(ghi)perylene
- * fluorene
- * phenanthrene
- * dibenzo(a,h)anthracene
- * indeno (1, 1, 3-cd)pyrene
- * pyrene
- 2,3,7,8-tetrachlorodibenzo-p-dioxin
- * acenaphthene
- * benzidine
- * 1,2,4-trichlorobenzene
- * hexachlorobenzene
- * hexachloroethane
- * bis (2-chloroethyl)ether
- * 2-chloronaphthalene
- * 1,2-dichlorobenzene
- * 1,3-dichlorobenzene
- * 1,4-dichlorobenzene
- * 3,3-dichlorobenzindine
- * 2,4-dinitrotoluene
- * 2,6-dinitrotoluene
- * 1,2-diphenylhydrazine (as azobenzene)
- * fluoranthene
- * 4-chlorophenyl phenyl ether
- anthanthrene
- benzo(e)pyrene
- dibenzo(a,H)pyrene
- dibenzo(a,i)pyrene
- dibenzo(c,g)carbozole
- 7,12 dimethyl benz(a)anthracene
- 3-methyl cholanthrene
- perylene

* Used in standard calibration mixture.

Infrared Analysis

1. Run polystyrene calibration film daily. Check against standard in manufacturer's manual. Also run a solvent and cell blank daily.

2. Transfer sample dropwise onto a central spot on the NaCl plate. Allow each drop to evaporate before adding another.

3. Mount NaCl plate in IR.

4. IR Parameters:

   Scan: 8 minutes

   Gain: 10 percent

   Chart setting: 90 percent, X 2

   Slit 2

   These parameters may be changed if the sample responds poorly.

5. Transfer sample back to vial quantitatively with the appropriate solvent. Refrigerate.

Elemental Analysis-Preparation of Filters and Filter Wash Samples

1. Weigh approximately 500 g of filter wash particulates to 0.1 mg, and place into a 125 ml wide mouth polyethylene bottle.

2. Using an "Exact-O-Knife" (brand name) cut the filters to the approximate weights. If there is more than one filter -- each filter must be cut proportionally to the percent of the total weights of the filters to reach 500 mg sample.

3. Record each weight.

4. Cut the weighed filters into thin strips and place them in the same 125 ml wide mouth polyethylene bottle.

5. Add 25 ml of freshly-made aqua regia. (1:3:1 HNO_3:HCl:H_2O) Cap and digest on a steam bath for 2-3 hours.

6. Cool, filter through No. 542 filter paper into 100 ml nalgene volumetric flask. Rinse throughly and make up to volume.

7. Transfer to the original 125 ml polyethylene bottom which has been rinsed clean.

Preparation for AA Parr Bomb

1. Weigh 1.0 g of sample (to nearest 0.1 mg) in a quartz crucible. Record weight.
2. Tie Pt fuse wire to both ignition poles and place quartz crucible inside its holder. Be sure that the Pt fuse wire makes contact with the sample pellet. (Care must be taken so that Pt wire does not blow sample out of the quartz crucible). If this happens, the pellet must be remade.
3. Add 10 ml of 1:1 $HNO_3:H_2O$ to the quartz container.
4. Moisten the O-ring around the top half of the bomb head with DI H_2O and seal the bomb.
5. Close the release valve and slowly add O_2 until 30 atm is reached.
6. Release pressure on O_2 tank. Disconnect hose.
7. Place bomb inside a water bucket (be sure to keep the bomb upright) with water going through bucket.
8. Connect fuse lines and ignite bomb (red light will blink on -- this gives the indication that the Pt wire was ignited).
9. Wait 10 minutes -- check bomb, when cool, remove from bucket and slowly release pressure valve (>2 minutes). When pressure is fully released, disassemble bomb.
10. Rinse quartz crucible with DI H_2O into a vycore crucible.
11. Pour contents into vycore and rinse quartz liners with DI H_2O into crucible also.
12. Cover vycore crucible with vycore lid and digest at low heat for 30 minutes.
13. Cool, filter using a plastic funnel through No. 542 filter paper into a nalgene 100 ml volumetric flask. Rinse and discard filter paper. Dilute to volume with DI H_2O.
14. Transfer to 100 ml narrow mouth polyethylene bottle which has been precleansed by inorganic cleanup method.
15. Label samples with proper ID and lab number.

TABLE E-3 AA METHODS

Element	Method	Wavelength (NM)	Slit (NM)	Lamp Power	Filter Used	Lamp Type	Sample Size	Integration (sec)	Standard I (ppb)	Standard II (ppb)	Char Temp (^0C)	Atom Temp (^0C)	Auto High Temperature	Sensitivity (1% Absorbance)(ppb)	Pyrolytic Graphite Tube
As	HGA	193.7	0.7 Alt	8 watts		EDL	20 ul	7	200	500	250	2700		4.3	
Ba	HGA	553.6	0.2 Alt	25 ma		HC	20 ul	7	200	500	1600	2800	Yes	5.0	Yes
Be	HGA	234.4	0.7 Alt	30 ma		HC	20 ul	7	10	20	1200	2800		0.15	
Bi	HGA	223.1	0.2 Alt	10 ma	Yes	HC	20 ul	7	50	200	900	2300	Yes	3.6	Yes
Cd	HGA	228.8	0.7 Alt	4 ma	Yes	HC	20 ul	7	10	20	250	2100		0.2	Yes
Co	HGA	240.7	0.2 Alt	30 ma		HC	20 ul	7	2	5	1000	2700		0.73	Yes
Cr	HGA	357.9	0.7 Alt	25 ma		HC	20 ul	7	50	200	1100	2700		0.57	Yes
Cu	HGA	324.7	0.7 Alt	15 ma		HC	20 ul	7	50	200	900	2700		0.73	Yes
Fe	HGA	248.3	0.2 Alt	30 ma		HC	20 ul	7	200	500	1100	2700	Yes	2.0	
Hg	Cold Vapor	253.7	0.7	6 ma	Yes	HC	25 ml	10	50	200				0.49	
Mo	HGA	313.3	0.2 Alt	30 ma		HC	20 ul	7	200	500	1800	2800	Yes	2.2	Yes
Mn	HGA	279.5	0.2 Alt	20 ma		HC	20 ul	7	2	5	1100	2700		0.20	Yes
Ni	HGA	232.0	0.2 Alt	25 ma		HC	20 ul	7	200	500	1000	2700		1.9	Yes
Pb	HGA	217.0	0.7 Alt	10 ma	Yes	HC	20 ul	7	50	200	700	2300		1.5	Yes
Sb	HGA	217.6	0.2 Alt	20 ma		HC	20 ul	7	200	500	900	2700		5.9	
Se	HGA	196.0	0.7 Alt	6 watts		EDL	20 ul	7	200	500	350	2700		2.3	
SN	HGA	224.6	0.7 Alt	30 ma	Yes	HC	20 ul	7	200	500	700	2700		4.2	
Te	HGA	214.0	0.2 Alt	30 ma		HC	20 ul	7	200	500	500	2700		4.2	
Ti	HGA	365.4	0.2 Alt	40 ma		HC	20 ul	7	200	500	1800	2800		15	Yes
Tl	HGA	276.8	0.7 Alt	20 ma		HC	20 ul	7	50	200	400	2300		4.6	Yes
U	Flame	591.5	0.2	--		--	0.5 ml	2	500,000	1,000,000					
V	HGA	318.4	0.2 Alt	40 ma		HC	20 ul	7	200	500	1700	2800	Yes	4.7	Yes
Zn	Flame	213.9	0.7	15 ma		HC	0.5 ml	2	100	300				20	
Zr	Flame	360.1	0.2	40 ma		HC	0.5 ml	2	500,000	1,000,000					

All readings in concentration. All use peak height and are background corrected.

Flame: Zn: acetylene:32 psig
air: 55 psig

U + Zr: acetylene:55 psig
NO_2:35 psig
U by flame emission

HGA: Dry 105^{0}C 30 sec (20 sec ramp)
Char 20 sec (10 sec ramp)
Atom 8 sec

Argon flow at 40
AS+Se have 0.1 ml of 1% $NiNO_3$ added to 1 ml of sample and standard
Sn uses a 30 sec Char (20 sec ramp)
Mo, Ti, and V use a 12 sec atom
Ti uses a flow of 80

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AA Preparation -- Particulates

1. Weigh 0.5 to 1.0 gram of sample into linear polyethylene bottle (LPE) to 0.1 mg.

2. Add 5.0 ml aqua regia (1:3:1; HNO_3 -HCl-H_2O) and 5.0 ml HF. Use only plastic for HF.

3. Screw cap on loosely and swirl until all of the sample is wetted.

4. Place bottle in a steam bath at approximately 70°C for 2 hours.

5. If solution is not clear, reheat for one-half hour.

6. Cool. Filter into 100 ml volumetric polyethylene flask. Rinse with deionized water and bring up to volume. Transfer to polyethylene bottle for storage. Label properly.

Mercury in Water - (Manual Cold Vapor Technique)

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100 percent recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organomercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

   1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 μg Hg/l can be achieved; concentrations below this level should be reported as < 0.2.

2. Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in an opened system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.

4. Interference

4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide to not interfere with the recovery of added inorganic mercury from distilled water.

4.2 Copper has also been reported to interfere; however copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganatge (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interferences from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present.

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (see Note 1.) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1-inch O.D. x 4-1/2 inch. The ends are ground perpendicular to the logitudinal axis and quartz windows (1 inch x 1/6 inch thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4 inch O.D.) are attached approximately 1/2 inch from each end. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-inch x 2-inch cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter. Capable of measuring an airflow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6 inch x 3/4 inch diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 2-8.

Note 2: In place of the magnesium perchlorate drying tube, small reading lamp with 60 W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (see note 3).

Note 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100.0 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5 percent solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium persulfate: 5 percent solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml.

1 ml = 1 mg Hg.

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15 percent nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 μg of mercury to a series of 300 ml BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc.

nitric acid (6.2) to each bottle. Add 15 ml of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottom to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standard and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

8. Reference

Methods for Chemical Analysis of Water and Waste, U.S. EPA Technological Transfer Office, 1974.

Boron Analysis

I. The fly ash is fused with Na_2CO_3. After dissolving the fusion mixture in HCl, the boric acid is extracted with 2-ethyl-1, 3-hexanediol and determine as the rosocyanine complex in 95 percent ethanol. This procedure is applicable for fly ash containing from 1 to 400 ppm Boron.

1. Apparatus and Reagents --

   - 10 ppm standard boron solution. Prepare by appropriate dilution of 1000 ppm stock boron solution, 2-ethyl-1, 3-hexanediol - 10 percent solution in chloroform.
   - Curcumin reagent, 0.375 percent (w/v). Dissolve 0.375 g curcumin in 100 ml glacial acetic acid; filter the solution and store it in a darkened polyethylene bottle.
   - Ethanol - 95 percent reagent grade.

- Sulfuric acid - high purity (Van Waters and Rogers ultrex grade).
- Na_2CO_3 - high purity (Van Waters and Rogers ultrex grade)
- 1N HCl. Transfer 28 ml high purity concentrated HCl to a 1-liter flask and fill to the mark with distilled water.

II. Analysis Procedure

For fly ash samples, weigh 0.1 g into platinum crucible and fuse with 1 g of NA_2CO_3. Then dissolve the mixture with 10 ml 1 N HCL and dilute to 100 ml.

For XAD-2 use Parr Bomb solution; for impingers use solution as is. Pipet 2 ml of this solution into a 10-ml glass, well washed centrife tube and extract by shaking with 2 ml, 2-ethyl-1, 3-hexandiol in $CHCl_3$. Syringe off the liquid phase and pipet 0.5 ml of the organic phase into a 50-ml Nalgene volumetric flask. Add 1 ml of curcumin reagent followed by 0.3 ml of conc. H_2SO_4 and allow to react for 15 minutes. Adjust the volume to 50 ml with reagent grade 95 percent ethanol and read absorbance at 550 mm against 95 percent ethanol. Run a reagent blank concurrently and subtract this absorbance from the sample absorbance. The boron concentration of the sample is calculated from a standard curve using the adjusted sample absorbance reading.

III. Standardization Procedures

Prepare standard solutions containing 0.0, 1.0, 2.0, and 3.0 ppm boron by successive dilution of the 10 ppm standard. Pipet 2 ml of prepared standard into a Nalgene centrifuge and proceed as per general procedure. Note that all apparatus is to be washed with 1:1 HNO_3.

ACCURACY ASSESSMENT -- BORON

Sample	CONC.	Amount Added	Amount Found	Percent Recovery X	$(\bar{X}-X)$	$(\bar{X}-X)^2$
4-Outlet-XAD	0.0	2	1.3	65	1	1
2-Inlet-1 μFlyash	0.4	1	0.9	64	2	4
2-Inlet-3 μFlyash	0.5	1	1.1	73	7	49
2-Inlet-10 μFlyash	0.5	1	1	67	1	1
4-Bottom Ash-Slurry	0.2	2	1.3	59	7	49
				328		104

$$X = \frac{\bar{\bar{X}}}{n} = \frac{328}{5} = 66$$

$$S = \sqrt{\frac{(\bar{X}-X)^2}{n-1}} = \sqrt{\frac{104}{4}} = 5$$

Accuracy = 66 percent Recovery
Precision = ±5 percent

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LEACHABLE ION ANALYSES - SASS SAMPLE STORAGE

H_2O leachate

at least 250 ml

AMMONIA

1. Destroy Cl_2 immediately with two drops of 0.1N Sodium Thiosulfate.
2. Store in glass or plastic at pH 6 (0.5 ml of 1 N. NCl per liter), tightly sealed.
3. Good for 24 hours.
4. Electrode method.

CHLORIDE

1. As is
2. Good for 7 days
3. Titration

CYANIDE

1. Destroy oxidizing agents wit ascorbic acid
2. Analyze immediately.
3. Electrode method.

FLUORIDE

1. Store in polyethylene at pH 5-8 4°C.
2. Good for 7 days.
3. Electrode method.

NITRATE

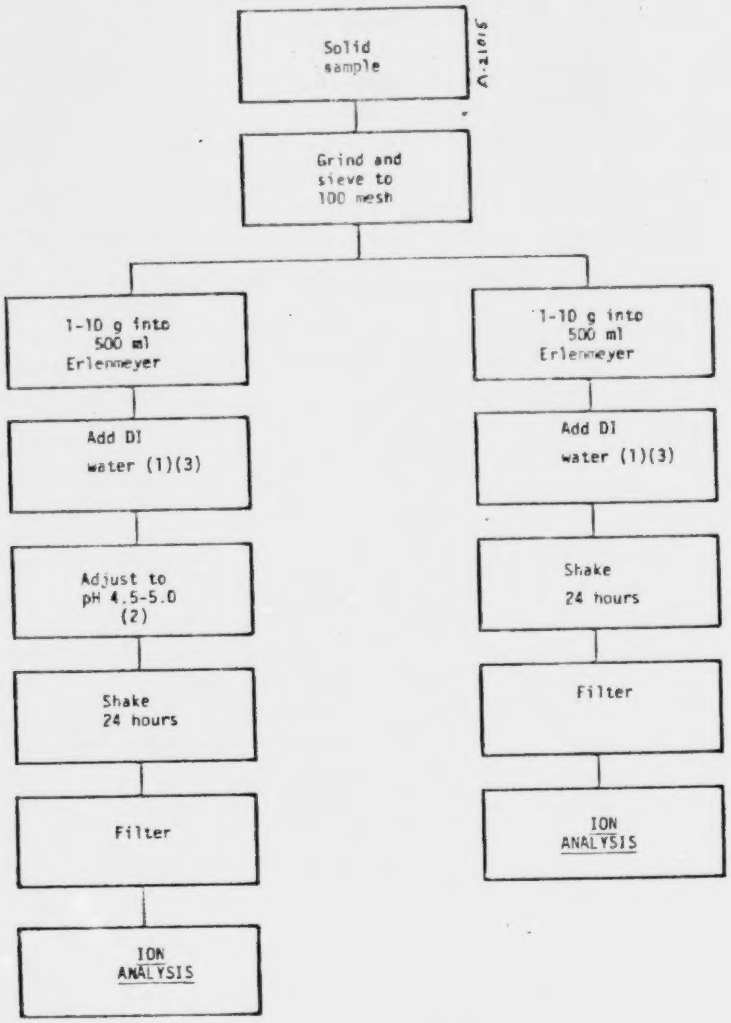
1. Adjust to pH 2, store at 4°C.
2. Good for 24 hours.
3. Colorimetric method.

SULFATE

1. Adjust to pH 2, store at 4°C.
2. Good for 7 days.
3. Titration

TABLE E-4

LEACHABLE ION ANALYSIS SCHEME


Solid sample
A-21015
Grind and sieve to 100 mesh
1-10 g into 500 ml Erlenmeyer
Add DI water (1)(3)
Adjust to pH 4.5-5.0 (2)
Shake 24 hours
Filter
ION ANALYSIS
1-10 g into 500 ml Erlenmeyer
Add DI water (1)(3)
Shake 24 hours
Filter
ION ANALYSIS

1. Maintain a 1:25 ash/water ratio.
2. Use 0.1 N HNO_3.
3. Use water reserved for ion analysis.

Ammonia Procedure

A. Equipment

1. Orion 701A pH/mV meter.
2. Magnetic stirrer.
3. Graph paper 4 cycle semilog.

B. Solutions

1. DI Water
2. 10M NaOH (40 g NaOH + 100 ml DI water).
3. Standard solution -- 1000 ppm N. (0.382 g NH_4Cl + 100 ml DI water).
4. Internal filling solution -- Orion No. 95-10-02.

C. Checking electrode slope. (Daily)

1. Put 100 ml DI water and 1 ml 10M NaOH in a beaker. Switch function to REL MV.
2. Pipette 1 ml of 1000 ppm standard into solution. Set the reading to 000.
3. Add 10 ml of 1000 ppm standard to the solution. Correct operation is indicated by a reading of 58 ± 1 mV at 20-25°C. If out of this range, see the trouble shooting check list in Instruction manual.

D. Direct Measurement Using 701A meter

CAUTION: Ammonia is a volatile species. Minimize loss by covering or capping all solutions until just before analysis. Minimize surface area:volume ratio.

1. Prepare 100 ppm, 10 ppm and 1 ppm by diluting the 1000 ppm stock standard.
2. Place electrode in the 10 ppm standard. Add 1 ml 10M NaOH to every 10 ml of standard. Set function switch to REL MV to 000. Use magnetic stirrer throughout procedure.
3. Rinse electrode and place in 1 ppm standard. Add 1 ml 10M NaOH to each 100 ml of standard. Stir. Record stable reading.
4. Repeat step 3 with 100 ppm standard.

5. Plot mV versus concentration on semilog paper. (Linear: mV, log: conc.) Previous standard curves are on file in the lab.

6. Rinse electrode. Place in sample. Sample must be at same temperature as the standards. Add 1 ml 10M NaOH to each 100 ml sample. pH should be 11-14. Stir, wait for stable reading and record. Calculate concentration using standard curve.

$$\text{ppm } NH_4 = 1.8 \times \text{ppm N}$$

E. Known Addition

1. Prepare a standard about 10x as concentrated as the concentration of the sample using 1000 ppm standard.

2. Add 1 ml 10M NaOH to 100 ml sample.

3. Turn function to REL MV and set to zero.

4. Pipet 10 ml of standard into sample. Record the potential, E. (Change in potential.)

5. From Table 4 in manual find the concentration ratio Q that corresponds to E.

$$C_o = QC_s$$

where:

C_o = total sample concentration

Q = reading from known addition table

C_s = concentration of added standard

6. If direct measurement and known addition agree within ± 4 percent the direct measurement is probably good. If known addition result is larger, then the sample may contain complexing agents. The analyst should check his/her technique; if results are reproducible, the concentration reported will be calculated from the known addition.

Chloride Procedure - Mercuric Nitrate Method

I. General Discussion

a. Principle: Chloride can be titrated with mercuric nitrage because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone indicates the end point of this titration by formation of a purple complex with the excess mercuric ions. The error in titration is about 1 percent of the volume of titrant used per change of 0.1 pH unit in the pH range 2.1 to 2.8. Because exact pH adjustment is not feasible except by use of a pH meter, it is felt that keeping within a range of ± 0.1 pH unit is sufficient for most water analyses. Therefore, in this method, a specific mixture of nitric acid and diphenylcarbazone is added to a water sample, adjusting the pH of most potable waters to pH 2.5 ± 0.1. A third substance in this alcoholic mixture, xylene cyanol FF, is used as a pH indicator and as a background color to facilitate end-point detection. The introduction of 10 mg sodium bicarbonate to both the blank and the standard titration provides a pH of 2.5 ± 0.1 when 1.0 ml indicator-acidifier reagent is added. Increasing the strength of the titrant and modifying the indicator mixture enable determination of the higher chloride concentrations common in wastewater.

b. Interference: Bromide and iodide are titrated with mercuric nitrate in the same manner as chloride. Chromate, ferric, and sulfite ions interfere when present in excess of 10 mg/l.

II. Reagents

a. Standard sodium chloride 0.0141 N.

b. Nitric acid, HNO_3, 0.1N.

c. Sodium hydroxide, NaOH, 0.1N.

d. Reagents for low-chloride titrations:

1. Indicator-Acidifier Reagent: The nitric acid concentration of this reagent is an important factor in the success of the determination and can be varied as indicated in a) or b) to suit the alkalinity range of the sample being titrated. Reagent a) contains sufficient nitric acid to neutralize a total alkalinity of 150 mg/l as $CaCO_3$ to the proper pH in a 100-ml sample.

a. Dissolve, in the order named, 250 mg s-diphenylcarbazone, 4.0 ml conc. HNO_3, and 30 mg xylene cyanol FF in 10 ml of 95 percent ethyl alcohol or isopropyl alcohol. Store in a dark bottle in a refrigerator. This reagent is not stable indefinitely. Deterioration causes a slow end point and high results.

b. Because pH control is critical in this method, adjust the pH of highly alkaline or acid samples to 2.5 ± 0.1 with 0.1 N HNO_3 or NaOH, not with Na_2CO_3. Use a pH meter with a nonchloride type of reference electrode for the pH adjustment. If only the usual chloride-type reference electrode is available for pH adjustment, determine the amount of acid or alkali required to achieve a pH of 2.5 ± 0.1 and discard this sample portion. Treat a separate sample portion with the determined amount of acid or alkali and continue the analysis to its prescribed end. Under these circumstances, omit the nitric acid from the indicator reagent to maintain the proper sample pH. Alternatively, vary the nitric acid concentration of the indicator-acidifier reagent to accommodate conditions wherein water samples of very high or very low alkalinity are being analyzed.

2. Standard mercuric nitrate titrant: 0.0141N: Dissolve 2.3 g $Hg(NO_3)$ or 2.5 g $Hg(NO_3)_2 \cdot H_2O$ in 100 ml distilled water containing 0.25 ml conc. HNO_3. Dilute to just under 1 liter. Make a preliminary standardization by following the procedure described in Paragraph IIIb. Use replicates containing 5.00 ml standard NaCl solution and 10 mg $NaHCO_3$ diluted to 100 ml with distilled water. Adjust the mercuric nitrate titrant to exactly 0.0141N and make a final standardization. Store away from the light in a dark bottle. Standard mercuric nitrate titrant, exactly 0.0141N, is equivalent to 500 µg Cl/1.00 ml.

e. Reagents for High-Chloride Titrations:

1. Mixed Indicator Reagent: Dissolve 5 g diphenylcarbazone powder and 0.5 g bromphenol blue powder in 750 ml 95 percent ethyl or isopropyl alcohol and dilute to 1 liter with ethyl or isopropyl alcohol.

2. Strong Standard Mercuric Nitrate Titrant, 0.141N: Dissolve 25 g $Hg(NO_3)_2 \cdot H_2O$ in 900 ml distilled water containing 5.0 ml conc. HNO_3. Dilute to just under 1 liter, and perform a preliminary standardization by following the procedure described in paragraph 3b. Use replicates containing 25.00 ml standard NaCl solution and 25 ml distilled water. Adjust the titrant to 0.141N and make a final standardization. The chloride equivalence of the titrant is 5.00 mg/1.00 ml.

III. PROCEDURE

a. Titration of low chloride concentrations: Use a 100-ml sample or smaller portion so that the chloride content is less than 10 mg.

Add 1.0 ml of indicator-acidifier reagent to the sample. (The color of the solution should be green-blue at this point. A light green indicates a pH of less than 2.0; a pure blue indicates a pH of more than 3.8. For most potable waters, the pH after this addition will be 2.5 ± 0.1. For highly alkaline or acid waters, adjust pH to about 8 before adding the indicator-acidifier reagent.)

Titrate the treated sample with 0.0141N mercuric nitrate titrant to a definite purple end point. The solution will turn from green-blue to blue a few drops from the end point.

Determine the blank by titrating 100 ml distilled water containing 10 mg $NaHCO_3$.

b. Titration of High Chloride Concentrations: Place 50.0 ml sample in a 150-ml beaker (5.00 ml sample may be used when more than 5 ml titrant are needed). Add approximately 0.5 ml mixed indicator reagent and mix well. The color should be purple. Add 0.1N HNO_3 dropwise until the color just turns yellow. Titrate with 0.141N mercuric nitrate titrant to the first permanent dark purple. Titrate a distilled water blank using the same procedure.

IV. CALCULATION

$$\text{mg/l Cl} = \frac{(A - B) \times N \times 35{,}450}{\text{ml sample}}$$

where A = ml titration for sample, B = ml titration for blank, and N = normality of $Hg(NO_3)_2$.

$$\text{mg/l NaCl} = \text{mg/l Cl} \times 1.65$$

V. PRECISION AND ACCURACY

A synthetic unknown sample containing 241 mg/l chloride, 108 mg/l Ca, 82 mg/l Mg. 3.1 mg/l K, 19.9 mg/l Na, 1.1 mg/l nitrate N, 0.25 mg/l nitrite N, 259 mg/l sulfate, and 42.5 mg/l total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard ceviation of 3.3 percent and a relative error of 2.9 percent.

VI. REFERENCE

Standard Methods for the Examination of Water and Wastewater 14th Edition, 1975, APHA.

CYANIDE

A. EQUIPMENT

1. pH meter
2. Cyanide standards 0.01 ppm to 1000 ppm standards made up and calibrated by EPA Method book, page 40.
3. Reagent C100CN (5N NaOH)

B. PROCEDURE

1. Standard Curve
   a. Connect electrodes to meter
   b. Pour first calibrating solution into a glass beaker. Using a magnetic stirring bar, stir at about 150 RPM. Add 2 parts reagent per 100 parts sample. (1 ml to 40 mls.)
   c. Read mV
   d. Rinse electrodes with DI water
   e. Read mV of second calibrating solution
   f. Plot mV versus CN^- concentration on semilog paper, the CN^- concentration on the log scale. Draw a straight line through the points. Previous standard curves are on file in the lab.

2. CN^- in unknown samples
   a. Add 2 parts C100CN to 100 parts of unknown sample
   b. Read mV of unknown solution
   c. Using graph prepared in step 1.f., read CN^- concentration of unknown.

3. Method of Known Addition

   a. Measure a known volume of sample (approximately 20 ml) into a beaker.
   b. Add 5 ml of the appropriate standard to the aliquot of unknown sample to attain a concentration level of 150 percent of sample level.
   c. Add 0.5 ml of C100CN to the 25 ml sample
   d. Read mV of unknown solution
   e. Calculate concentration and recovery. Determine if any interferences are present. If recoveries are outside 100 ± 20 percent, use values calculated by known addition.

NOTE: Calibrating solution and unknown solutions must be the same temperature.

FLUORIDE PROCEDURE

A. EQUIPMENT

1. pH meter Orion 701A.
2. Combined reference electrode; fluoride electrode
3. Magnetic stirrer
4. 4 cycle semilog paper
5. Plastic labware

B. SOLUTIONS REQUIRED

1. Standard solutions, 100 ppm, 10 ppm, 1 ppm, F as NaF
2. Total ionic strength adjustor (TISABII-57 ml acetic acid, 58 g NaCl, and 4 g CDTA to 500 ml DI water. Dissolve. Cool. Add 5 M NaOH to pH 5.0-5.5. Dilute to 1 liter).

C. CHECKING ELECTRODE SLOPE (DAILY)

1. Put 50 ml DI water and 50 ml TISABII into 150 ml plastic beaker. Turn function switch to mV.
2. Pipet 1 ml of 100 ppm standard into solution. Stir thoroughly. Record mV.
3. Add 10 ml of 100 ppm standard. Read electrode potential in mV. Determine the difference between the first and second potential. The correct electrode operation is indicated by a difference of 56 ± 1 mV at 20-25 C.
4. If the potential change is below 54 mV, see the troubleshooting check list in the manufacturer's manual.

D. DIRECT MEASUREMENT OF UNKNOWNS

1. Prepare a standard curve of 100, 10, and 1 ppm by adding 50 ml TISABII to 50 ml of each standard. These solutions, though diluted with TISABII, should be designated "100 ppm," "10 ppm," and "1 ppm."
2. Place electrode in the 10 ppm standard. Switch to REL MV. Set the reading to 000.
   Use magnetic stirrer while taking all readings, but avoid creating a vortex.
3. Rinse electrode with DI water and blot dry with Kim wipes. Place in the 1 ppm standard. Wait for stable reading and record.
4. Rinse electrode and blot dry. Place electrode in 100 ppm standard. Wait for stable reading and record.
5. Plot mV readings on 4 cycle semilog paper (linear:mV; log, conc.) Standard curves are on file in the lab.
6. Transfer 50 ml sample or less to a plastic beaker. Samples should be at same temperature as standards. Add 50 ml or less of TISABII in 1:1 proportion to reach pH 5-6.
7. Rinse electrode, blot dry and place in sample. Record mV reading. Determine the unknown concentration from the calibration curve.

E. KNOWN ADDITION

1. Prepare standard about 10 times as concentrated as the sample concentration by diluting 100 ppm standard.
2. Add 50 ml TISABII to 50 ml standard.

3. Turn function switch to REL mV. Set reading to 000.
4. Pipet 10 ml of standard into sample. Record the potential, E. (Change in potential.)
5. From Table 3 in instruction manual find concentration ratio, Q, that corresponds to the change in potential, E.

   $$C^o = QC_s$$

   where:

   C^o = total sample concentration

   Q = reading from known addition table

   C_s = concentration of added standard
6. Check against direct measurement. If they agree within ±4 percent the direct measurements are probably good. If known addition results is much larger than direct measurement, sample probably contains complexing agents. Values reported should be calculated by known addition.

NOTE: OH^- ion is an electrode interference

NITRATE

1. REAGENTS

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available, otherwise use the best available grade.

1.1 Sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide freshly prepared from 30 percent hydrogen peroxide solution. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

1.2 Sample Recovery. Two reagents are required for sample recovery.

1.2.1 Sodium Hydroxide (1N). Dissolve 40 g NaOH in deionized, distilled water and dilute to 1 liter.

1.2.2 Water. Deionized, distilled to conform to ASTM specification D1139 74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

1.3 Analysis. For the analysis, the following reagents are required:

1.3.1 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

1.3.2 Phenol. White solid.

1.3.3 Sulfuric Acid. Concentrated, 95 percent minimum assay. HANDLE WITH CAUTION.

1.3.4 Potassium Nitrate. Dried at 105 to 110°C (220 to 230°F) for a minimum of 2 hours just prior to preparation of standard solution.

1.3.5 Standard KNO_2 Solution. Dissolve exactly 2.198 g of dried potassium nitrate (KNO_2) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1.00-ml volumentric flask.

1.3.6 Working Standard KNO_3 Solution. Dilute 10 ml of standard solution to 100 ml with deionized, distilled water. One milliliter of the working standard solution is equivalent to 100 µg nitrogen dioxide (NO_2).

1.3.7 Water. Deionized, distilled as in Section 1.2.2.

1.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100°C (212°F) for 2 hours. Store in a dark. stoppered bottle.

2. PROCEDURE

Pipette an aliquot into the porcelain evaporating dish. Adjust to ph 9-12 by adding NaOH (2N) dropwise. Evaporate the aliquot to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml deionized, distilled water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator), as follows: filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with deionized, distilled water. Mix the contents of the flask thoroughly, and measure the absorbance at 410 nm using the bland solution as a zero reference. Dilute the sample and the blank with equal volumes of deionized, distilled water if the absorbance exceeds the absorbance of the 400 µg NO_2 standard (see 3.1 under "Calibration" in next section).

3. CALIBRATION

3.1 Determination of Spectrophotometer Calibration Factor K. Add 0.0 ml, 2 ml, 4 ml, 6 ml, and 8 ml of the KNO_3, working standard solution (1 ml =μ100 g NO_3) to a series of five 50-ml volumetric flasks. To each flask add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1 N) dropwise until the pH is between 9 and 12 (about 35 drops each). Dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25 ml aliquot of each solution into a separate porcelain evaporation dish. Beginning with the evaporation step, follow the analysis procedure of Section 2, until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at 410 nm. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{(Equation 1)}$$

where:

K_c = Calibration factor
K_1 = Absorbance of the 100-μg NO_2 standard
K_2 = Absorbance of the 200-μg NO_2 standard
K_3 = Absorbance of the 300-μg NO_2 standard
K_4 = Absorbance of the 400-μg NO_2 standard

4. CALCULATIONS

Carry out the calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

4.1 Nomenclature

A = Absorbance of sample
F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration)
K_c = Spectrophotometer calibration factor
m = Total μg NO_2 per sample

4.3 Total μg NO_2 per sample.

$$M = [\text{Total volume (ml)}/\text{aliquot volume (ml)}]\ (K_cAF) \qquad \text{(Equation 2)}$$

$$1.35\ m = \mu g\ NO_3 \qquad \text{(Equation 3)}$$

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SULFATE ANALYSIS

I. EQUIPMENT AND REAGENTS

1. LC columns, 300 mm high x 10.5 mm wide, 250 ml solvent reservoir.
2. 10 or 25 ml buret.
3. Dowex 50W-X8 (100-200 mesh) ion exchange resin
4. Barium Perchlorate ($Ba(ClO_4)_2 \cdot 3H_2O$), 0.0100N.
   Dissolve 1.95 grams (dry) in 200 mls DI water, dilute to one liter with 800 ml isopropanol. Protect from evaporation. Standardize daily against H_2SO_4 and/or standard Na_2SO_4 solution.
5. Standard Na_2SO_4 solution.
   Weigh 200 mg dry Na_2SO_4. Dilute to 100 ml with DI water.
6. Isopropanol (IPA)
7. Thorin indicator (p.2 g dilutes to 100 ml with DI Water)
8. Standard H_2SO_4 0.0100 N.

II. METHOD

1. If samples are passed through ion-exchange resin:
   - A. Thoroughly wash, rinse, and dry ion-exchange columns. Rinse with IPA. Dry.
   - B. Make a slurry of Dowex resin and DI water. Plug column with small amount of glass wool. Pour a column 2 to 3 inches high. Allow to settle. Rinse with DI water till the washes are clear.
   - C. Add 10 mls sample to the top of the column. Elute, catching in a 250-500 ml Erlenmeyer flask. Add 10 ml DI water. Elute.
2. If samples are analyzed without ion-exchange treatment, add DI water to the sample aliquot to make 20 ml.
3. Add 80 mls IPA to the 20 mls of sample solution. Add 2-4 drops thorin indicator. Titrate with Barium solution to a permanent salmon-pink color. Be consistent in end-point definition by comparing samples with blanks.

III. CALCULATION

1. Total mg SO_4 =

$$\frac{(\text{N of } Ba(ClO_4)_2 \cdot 3H_2O)(\text{titer ml} - \text{blank ml})(48)(\text{total volume})}{\text{Sample aliquot volume}}$$

SULFATE QUALITY CONTROL PROGRAM

1. Analyze appropriate blanks.
   - A. Reagent blank.

B. Solution blanks for each type of sample:
   1. Leachates
   2. 3 percent H_2O_2 (Method 5/8)
   3. 80 percent IPA (Method 5/8)

C. Filter blanks leached by sulfate particulate method.

2. One sample from each type in a batch shall be analyzed in duplicate and spiked to determine recovery. Alternatively, one sample of each sample type in seven shall be run in duplicate and spiked.

3. Duplicate titrations must agree within ±0.5 ml of 0.01N titrant or be repeated.

4. Spike and recovery procedure

   Add a known amount of sulfate (standard solutions) to a sample aliquot. Final sulfate concentration should be 150 percent of sample concentration. If samples are run through the ion-exchange column, spikes should be run similarly.

   Titrate spikes as per sulfate procedure. Calculate recovery.

$$\% \text{ recovery} = \left(\frac{\text{mg/sulfate found}}{\text{mg sulfate actual}}\right) \times 100$$

mg sulfate (found) = (titer of spike - titer of blank) (N) (48)
mg sulfuate (actual) = (ml sample)(sample concentration mg/ml) + (ml acid)(N acid) (48)

   If recovery is outside the range 100 percent ±5 percent, check calculations and duplicate data. If error is not mathematical, repeat spike.

5. If a detection limit is requested, a solution with the value given must have been prepared and titrated by the sulfate procedure.

6. Standardization of titrant must be done daily against at least two standard sulfate solutions. Titers must agree within ±0.1 ml. Regeant blank titers should be subtracted from titer values.

7. Average blank titers are 0.1 to 0.2 ml.

a5358

APPENDIX F

RESULTS OF SASS INFRA-RED (IR) ANALYSIS

This Appendix contains the IR data referenced in Section 3.7.3 of this report.

f5358

TABLE F-1

IR ANALYSIS

IR Spectrum Reference No.: 12/13/7

Sample ID: Test 3-Inlet 10 μm + 3 μm Fly Ash

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
3800-3100	w	Broad, carboxylic acid
2960, 2920, 2850	s	Alphatic C-H
1740	s	C=O
1460	m	Alkanes
960	s	Possibly due to para substituted phenol

2. Unassigned Weak Bands: 1500 cm^{-1}, 1300 cm^{-1}, 1100 cm^{-1},
1010 cm^{-1}, 1380 cm^{-1}, 1140 cm^{-1}
1190 cm^{-1}, 1240 cm^{-1},

3. Other Remarks: Phthalate contamination.

e5358

TABLE F-2

IR ANALYSIS

IR Spectrum Reference No.: 12/13/19

Sample ID: Test 3-Inlet-XAD-2 Resin

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
2960, 2920, 2850	s	Aliphatic C-H/(in blank also)
1740	m	C=O/(in blank)
1260	m	Unassigned/(in blank)
800	w	Unassigned

2. Unassigned Weak Bands:

3. Other Remarks: Phthalate contamination.

d5358

TABLE F-3

IR ANALYSIS

IR Spectrum Reference No.: 12-29-4

Sample ID: Test 3-Inlet-XAD-2 Resin LCl

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
2960, 2920, 2840	s	Aliphatic C-H

2. Unassigned Weak Bands:

3. Other Remarks: Phthalate contamination.

d5358

TABLE F-4

IR ANALYSIS

IR Spectrum Reference No.: 12-29-5

Sample ID: Test 3-Inlet-XAD-2 Resin LC2

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
2920, 2840	s	Aliphatic C-H/weak spectrum

2. Unassigned Weak Bands:

4. Other Remarks: Phthalate contamination.

d5358

TABLE F-5

IR ANALYSIS

IR Spectrum Reference No.: 12-29-6

Sample ID: Test 3-Inlet-XAD-2 Resin LC3

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
2960	s	Aliphatic C-H
1150-970	m	Unassigned vibration

2. Unassigned Weak Bands: 1250 cm^{-1}

3. Other Remarks: Phthalate contamination.

d5358

TABLE F-6

IR ANALYSIS

IR Spectrum Reference No.: 12-29-7

Sample ID: Test 3-Inlet-XAD-2 Resin LC4

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
2960, 2920, 2840	s	Aliphatic C-H/(in blank)
1750	m	C=O/broad
1650, 1630, 1580	m	Unassigned
1460	m	CH_2, alkene
1440	m	Alkanes
1250	m	c-o
1100-1000	m	Unassigned/broad
800	m	Unassigned
3350	w	OH/broad

2. Unassigned Weak Bands: 1295 cm^{-1}, 1160 cm^{-1}, 890 cm^{-1}

3. Other Remarks: Phthalate contamination.

d5358

TABLE F-7

IR ANALYSIS

IR Spectrum Reference No.: 12-29-8

Sample ID: Test 3-Inlet-XAD-2 Resin LC5

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments

2. Unassigned Weak Bands:

3. Other Remarks: No peaks

d5358

TABLE F-8

IR ANALYSIS

IR Spectrum Reference No.: 12-29-9

Sample ID: Test 3-Inlet-XAD-2 Resin LC6

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
3680-3140	s	OH broad/(in blank)
3060	w	Aromatic C-H
2960, 2920, 2850	s	Aliphatic C-H
1720	s	C=0/(in blank)
1600, 1880	m	Aromatic ring
1450	m	CH_2 alkanes shoulder/(in blank)
1370	m	Alkanes/(in blank)
1270	m	C=0
1110	m	Unassigned
1060	m	Unassigned
740, 710	w	Aromatic substitution

2. Unassigned Weak Bands: 960 cm^{-1}, 920 cm^{-1}, 800 cm^{-1}

3. Other Remarks: Phthalate contamination.

d5358

TABLE F-9

IR ANALYSIS

IR Spectrum Reference No.: 12-29-10

Sample ID: Test 3-Inlet-XAD-2 Resin LC7

Project No.: 306785

1. Major Peaks and Assignments:

cm^{-1}	Intensity	Assignment/Comments

2. Unassigned Weak Bands:

3. Other Remarks: No peaks

d5358

TABLE F-10

IR ANALYSIS

IR Spectrum Reference No.: 1-9-8

Sample ID: XAD-2 Resin Blank LC1

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
3920, 2840		Aliphatic C-H/weak spectrum

2. Unassigned Weak Bands:

3. Other Remarks: Phthalate contamination.

TABLE F-11

IR ANALYSIS

IR Spectrum Reference No.: 1-9-10

Sample ID: XAD-2 Resin Blank LC3

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments

2. Unassigned Weak Bands:

3. Other Remarks: No peaks

TABLE F-12

IR ANALYSIS

IR Spectrum Reference No.: 1-9-9

Sample ID: XAD-2 Resin Blank LC2

Project No.: 306725

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments

2. Unassigned Weak Bands:

3. Other Remarks: No peaks

TABLE F-13

IR ANALYSIS

IR Spectrum Reference No.: 1-9-11

Sample ID: XAD-3 Resin Blank LC4

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
2960,2920,2840		Aliphatic C-H/weak spectrum

2. Unassigned Weak Bands:

3. Other Remarks: Phthalate contamination

d5358

TABLE F-14

IR ANALYSIS

IR Spectrum Reference No.: 1-9-12

Sample ID: XAD-2 Resin Blank LC5

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments

2. Unassigned Weak Bands:

3. Other Remarks: No peaks

d5358

TABLE F-15

IR ANALYSIS

IR Spectrum Reference No.: 1-9-14

Sample ID: XAD-2 Resin Blank LC6

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
3600-3000	w	OH/broad
2960, 2920, 2850	s	Aliphatic/C-H
1740	m	C=O/broad
1460	m	CH_2 alkanes
1370	m	Alkanes
1140	w	Unassigned/broad

2. Unassigned Weak Bands: 1100 cm^{-1}, 1000 cm^{-1}, 960 cm^{-1}

3. Other Remarks: Phthalate contamination.

d5358

TABLE F-16

IR ANALYSIS

IR Spectrum Reference No.: 1-9-15

Sample ID: XAD-2 Resin Blank LC7

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments

2. Unassigned Weak Bands:

3. Other Remarks: No peaks

f5358

TABLE F-17

IR ANALYSIS

IR Spectrum Reference No.: 12/13/10

Sample ID: Test 4-Inlet 10 μm + 3 μm Fly Ash

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
2960, 2920, 2850	s	Aliphatic C-H
1740	s	Broad C=O
1750	m	Alkanes
1260	s	Possibly due to ester (C-O)
1100	s	Broad, unassigned
1010	s	Broad, over 1100 cm^{-1}
800	s	Ether

2. Unassigned Weak Bands: 700 cm^{-1}

3. Other Remarks:

d5358

TABLE F-18

IR ANALYSIS

IR Spectrum Reference No.: 12/13/9

Sample ID: Test 4-Inlet-XAD-2 Resin

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments

2. Unassigned Weak Bands:

3. Other Remarks: No Peaks

d5358

TABLE F-19

IR ANALYSIS

IR Spectrum Reference No.: 12/12/3

Sample ID: Test 4-XAD-2-Blank

Project No.: 306785

1. Major Peaks and Assignment:

cm^{-1}	Intensity	Assignment/Comments
3600-3100	m	Broad, carboxylic acid
2960, 2920, 2830	s	Alphatic C-H
1740	s	Carbonyl
1450	m	CH_2 or alkane
1110	s	C=0
800	w	Assigned

2. Unassigned Weak Bands: 1600 cm^{-1}, 1380 cm^{-1}, 1200 cm^{1}, 1010 cm^{-1}, 640 cm^{-1}, 620 cm^{-1}

3. Other Remarks: Phthalate Contamination

e5358

APPENDIX G

ULTRASONIC THICKNESS GAUGE

USERS MANUAL

(SELECTED PAGES)

During this project, an ultrasonic device was used to measure the thickness of the walls of the boiler water tubes. The KB CL-204 is a portable battery operated thickness gauge which gives a digital display of the thickness of a specimen in inches by measuring the time required for the echo of a pulsed sound wave to return from the unseen far (inside) wall of the tube. This signal is processed and the operator sees a four place digital display of tube wall thickness in inches of the form 0.XXXX, where the right-most digit has units of ten-thousandths of an inch.

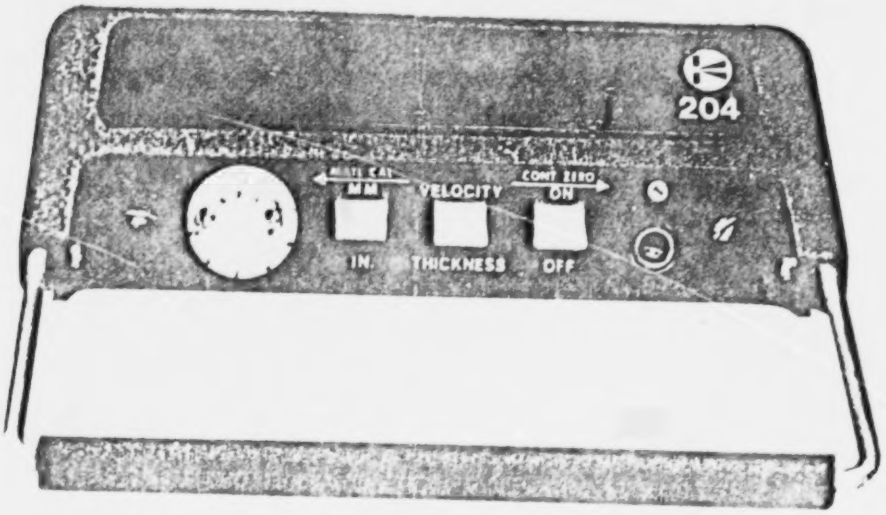
The following are selected pages from the technical manual of operating instructions for that instrument. For additional information, the interested reader may wish to contact the manufacturer directly. (The address and other necessary information is contained in this appendix.)

TECHNICAL MANUAL

VOL. 1. OPERATING INSTRUCTIONS
VOL. 2. SERVICE INSTRUCTIONS

MODEL CL 204

Ultrasonic Pulse-Echo Thickness Gage
with
Digital Thickness/Velocity Readout


204
MULT CAL
MM
VELOCITY
CONT ZERO
ON
IN.
THICKNESS
OFF

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First Edition First Printing

NOVEMBER 1975

TABLE OF CONTENTS

Section Page

I INTRODUCTION .1-1

1-1. Scope .1-1
1-3. Purpose and Use .1-1
1-5. Description .1-1
1-7. Technical Data .1-1

II THEORY OF OPERATION .2-1

2-1. Ultrasonics .2-1
2-3. Pulse-Echo Measurement .2-1
2-5. Sound Velocity .2-1
2-8. Echo Timing .2-1

III OPERATION .3-1

3-1. Unpacking and Installation .3-1
3-6. Initial Checkout .3-5
3-10. Start Up .3-6
3-12. Battery Indicator and Charging .3-11
3-17. Couplant .3-13
3-19. Calibrating .3-14
3-24. Taking Measurements .3-15
3-28. In Case of Difficulty .3-16

SECTION II

THEORY OF OPERATION

2-1. ULTRASONICS

2-2. *Ultrasonics* refers to sound above the range of human hearing. Initially, this meant those frequencies just above approximately 20 kHz, but modern ultrasonic instruments operate up to frequencies of 25 mHz. Ultrasound can be propagated with low loss in most materials that are good conductors of sound, such as metals, water, and other liquids and solids. Compared to the loss in propagation through liquids or metals, propagation of ultrasound through gas is quite attenuative. At the boundary between a solid and a gas, little ultrasound can be transmitted; most of the energy is reflected. This phenomenon is important in the application of ultrasonics to material testing, particularly to ultrasonic thickness measurement using the pulse-echo method.

2-3. PULSE-ECHO MEASUREMENT

2-4. Measurement of thickness with the CL 204 is accomplished with the pulse-echo method. Probably the most familiar examples of pulse-echo measurement are radar and sonar. In radar, a radio wave pulse is emitted from an antenna and propagates until striking a reflecting target. The pulse is reflected back to its origin, where it is received and detected. By knowing the rate at which the pulse travelled through the atmosphere and the time interval between its departure and return, the distance at which the reflecting target lies from the antenna can be easily found. Sonar functions in a similar manner, using low audio frequency pulses and water as the propagation medium. As in the preceding examples, thickness measurement is accomplished with ultrasonics by using the pulse-echo method. A pulse of ultrasound is emitted by a probe which is held in contact with the testpiece to be measured. The ultrasound enters the testpiece and travels through it until reaching the backwall. Because the backwall forms a boundary between solid and gas, i.e., the testpiece and the atmosphere, almost all the energy will be reflected back towards the probe. In the intervals between pulsings, the probe acts as a receiver, listening for the returning echoes. The time interval between pulse and echo is proportional to twice the thickness of the testpiece, since the sound has made a round trip. Therefore, if the speed at which the sound travelled in the testpiece is known, the thickness of the testpiece can be computed.

Appendix H

Foster Wheeler Evaluation of Tubewall Corrosion

The following pages contain conclusions reached by Foster Wheeler Energy Corporation, the manufacturer of the Crist No. 7 boiler.

The data used to support these conclusions came from Exxon as well as from FWEC's own sources.

EVALUATION OF TUBEWALL CORROSION
DURING LONG-TERM REDUCED NO_x FIRING

Prepared For

EXXON RESEARCH AND ENGINEERING CO.

FWEC Reference No. 7-26-2826

Exxon Reference No. ESC-25

EPA No. 68-02-1415

Program Manager: J. Vatsky

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a5358

TABLE OF CONTENTS (FOR APPENDIX H)

SECTION	TITLE	PAGE NO.
	LIST OF TABLES	244
	LIST OF FIGURES	245
1.0	INTRODUCTION	247
2.0	TEST PROGRAM OUTLINE	250
3.0	TEST PANEL ANALYSIS	253
	3.1 Chemical Analysis	253
	3.2 Visual/Macroscopic Examination	253
	3.3 Microscopic Examination	254
	3.4 Hardness Measurements	255
4.0	TUBEWALL THICKNESS MEASUREMENTS	256
5.0	DISCUSSION OF LABORATORY EVALUATIONS	257
6.0	CONCLUSION AND RECOMMENDATIONS	259

a5358

LIST OF TABLES (FOR APPENDIX H)

NUMBER	TITLE	PAGE
1	Chemical Analysis of Corrosion Products	263
2	Summary of Ultrasonically Measured Tube Wall Thickness Changes Occurring as a Result of Test Exposure	264
3	Ultrasonic Tube Wall Thickness Measurements Panel No. 1	265
4	Ultrasonic Tube Wall Thickness Measurements Panel No. 2	267
5	Ultrasonic Tube Wall Thickness Measurements Panel No. 3	269
6	Ultrasonic Tube Wall Thickness Measurements Panel No. 4	271
7	Ultrasonic Tube Wall Thickness Measurements Panel No. 5	273
8	Ultrasonic Tube Wall Thickness Measurements Panel No. 6	275
9	Ultrasonic Tube Wall Thickness Measurements Panel No. 7	277
10	Ultrasonic Tube Wall Thickness Measurements Panel No. 8	279
11	Summary of Tube Wall, OD Micrometer Measurements and Hardness Measurements	281

a5358

LIST OF FIGURES (FOR APPENDIX H)

NUMBER	TITLE	PAGE
1	Photograph: As Received, Initial Test Panels 3 and 5	282
2	Photograph: As Received, Initial Test Panels 4 and 1	283
3	Photograph: As Received, Initial Test Panels 6 and 7	284
4	Photograph: As Received, Initial Test Panels 2 and 8	285
5	Photograph: As Received, Replacement Test Panels 3 and 5	286
6	Photograph: As Received, Replacement Test Panels 4 and 1	287
7	Photograph: As Received, Replacement Test Panels 6 and 7	288
8	Photograph: As Received, Replacement Test Panels 2 and 8	289
9	Photograph: Initial Test Panel 3 After Cleaning	290
10	Photograph: Initial Test Panel 4 After Cleaning	291
11	Photograph: Initial Test Panel 5 After Cleaning	292
12	Photograph: Initial Test Panel 6 After Cleaning	293
13	Photograph: Initial Test Panel 7 After Cleaning	294
14	Photograph: Replacement Test Panel 3 After Cleaning	295
15	Photograph: Replacement Test Panel 4 After Cleaning	296
16	Photograph: Replacement Test Panel 5 After Cleaning	297
17	Photograph: Replacement Test Panel 6 After Cleaning	298
18	Photograph: Replacement Test Panel 7 After Cleaning	299
19	Photograph: Transverse Sections Initial Test Panel 3	300
20	Photograph: Transverse Sections Initial Test Panel 4	301
21	Photograph: Transverse Sections Initial Test Panel 5	302
22	Photograph: Transverse Sections Initial Test Panel 6	303

LIST OF FIGURES (FOR APPENDIX H)
(CONTINUED)

NUMBER	TITLE	PAGE
23	Photograph: Transverse Sections Initial Test Panel 7	304
24	Photograph: Transverse Sections Replacement Test Panel 3	305
25	Photograph: Transverse Sections Replacement Test Panel 4	306
26	Photograph: Transverse Sections Replacement Test Panel 5	307
27	Photograph: Transverse Sections Replacement Test Panel 6	308
28	Photograph: Transverse Sections Replacement Test Panel 7	309
29	Photomicrograph: Original Boiler Tubing, Panel 6	310
30	Photomicrograph: Original Boiler Tubing, Panel 6 at High Magnification	311
31	Photomicrograph: Initial Test Panel 6, Tube No. 1	312
32	Photomicrograph: Initial Test Panel 6, Tube No. 1, at High Magnification	313
33	Photomicrograph: Initial Test Panel 6, Tube No. 2	314
34	Photomicrograph: Initial Test Panel 6, Tube No. 2, at High Magnification	315
35	Photomicrograph: Replacement Test Panel 6, Tube No. 1	316
36	Photomicrograph: Replacement Test Panel 6, Tube No. 1, at High Magnification	317

1.0 INTRODUCTION

The investigation of the effect of staged combustion on the corrosion rate of waterwall tubes in a large utility steam generator was performed by Exxon Research and Engineering Co. (ERE) with support from Foster Wheeler Energy Corp. (FWEC). FWEC's responsibility can be summarized as follows:

1. Provide engineering support and advice for preparing statistical test plans.
2. Perform ultrasonic tube-wall thickness measurements on the boiler's walls.
3. Prepare, characterize and install test panels at appropriate locations within the walls.
4. Perform laboratory evaluations of the test panels after removal (wall thickness, metallurgical and chemical analyses)
5. Evaluate the resultant data and provide a manufacturers viewpoint of the significance of those results.

In-situ tube wall thickness measurements were made at six levels on all four walls. Four sets of data were taken over a period of two years, including a baseline interval and reduced NO_x (staging) intervals. The ultrasonic data was provided to ERE for statistical analysis.

Two sets of 8 waterwall tube test panels, each approximately 5 ft. long and containing five 3" OD x 0.284" min. wall steel tubes were removed from Gulf Power Co. Crist Unit No. 7 located in Pensacola, Florida and submitted to the Foster Wheeler Development Corp. (FWDC) laboratory for metallurgical examination. The metallurgical examination was designed to determine the effects of reduced NO_x operation upon carbon steel (SA 210A) and 1/2 Cr and 1/2 Mo (SA 213-T2) waterwall tubing subjected to normal unit operational temperatures of approximately 600-700°F and pressures of 2600 psig.

The first set of 8 test panels submitted were removed in October 1977 and contained 3 of the original boiler tubes which were in service approximately 5 years, and 2 tubes which were part of 5 tube test panels installed in the unit in May 1976. The 2 tubes were in service approximately 17 months.

The second set of 8 test panels were removed in May 1978 and consisted of 3 tubes remaining from the initial test panels and 2 tubes from the 5 tube replacement panels installed in October 1977. The 3 initial test panel tubes were in service approximately 23 months and the replacement panel tubes approximately 6 months.

The study included visual and macroscopic examinations of tube wastage processes occurring on the outside surfaces of tubes in selected panels; selective chemical analyses of corrosion products removed from tubing fireside surfaces; performance of hardness measurements; tube wall thickness measurements by ultrasonic and micrometer methods and microstructural examination of the hot and cold faces of selected tube sections.

The examination showed that tubes located in all eight replacement panels which were exposed for 6 months and tubes in Initial Test Panel Nos. 1, 2, 7, and 8 suffered no significant tube wall losses as a consequence of furnace exposure during the 17 and 23 month test periods. Tubes in Initial Test Panel No. 5 exhibited slight wall losses of several mils, while Initial Test Panel No. 6 suffered tube wall losses of approximately 7-11 mils; tubes in Panel No. 3 approximately 11-15 mils and most tubes in Panel No. 4 slightly higher. Anomalously, one tube in Panel No. 4 showed tube wall losses of 50 mils while another tube in the same test panel showed 6 mils increase in the tube wall thickness.

The examination also showed that tubing material was not overheated during unit operation; that there were no significant differences in the corrosion behavior of the carbon steel and 1/2Cr-1/2Mo tubing alloys; and that environmental conditions may have been less corrosive during the last year of operation.

2.0 TEST PROGRAM OUTLINE

The steam generator is a natural circulation reheat unit which produces 3,800,000 lb/hr of superheated steam at 1005°F. Superheat steam temperature control is via a spray atemperation system while reheat temperature control is via a parallel pass convection section with proportioning gas dampers. This temperature control system allows some flexibility in combustion system modification without adversely affecting unit performance.

The method of NO_x reduction available,without requiring hardware modifications,was biased firing of the burner levels. This consists of firing the lower two burner levels at full pulverizer capability while operating the top burner level at the minimum pulverizer loads possible for maintaining boiler steam load. Also the top level registers were set at a more open position than the lower two levels. However, for the range of register settings used there was only a negligible effect on NO_x. Pulverizer biasing provided most of the NO_x reduction.

Design excess air for this unit is 18% or approximately 3.4% excess oxygen (O_2). However, due to lack of CO monitoring equipment the operators normally maintain the O_2 level at approximately 4.5%. This results in abnormally high NO_x emissions as compared to boiler design conditions. Reliable O_2 and CO monitors are required to enable a boiler to operate reliably and continuously at design conditions.

It is well known that further reductions in NO_x can be obtained by reducing excess O_2 below the design level with a possible improvement in unit efficiency due to the decrease in sensible heat loss to the stack (decreased gas flow). There are, however, two important limitations on low excess air firing which must be evaluated: possible increases in unburned carbon levels and failure to make steam temperature. Increased boiler efficiency at low excess air is a fictitious gain if steam temperature is not maintained: low steam temperature results in higher station heat rate.

The primary goal of this program was to evaluate and quantify the effects of substoichiometric burner operation on tubewall corrosion. It was agreed, initially, that biased firing would be used since this was the least costly method of reducing lower furnace stoichiometry. But this method has a number of drawbacks:

- Pulverizer load must be dedicated to reducing NO_x emissions rather than meeting varying steam generator requirements
- Removing any lower mill from service changes the lower furnace stoichiometry
- Without incorporating flow measuring devices at the burners the actual stoichiometries and their variations with time could not be known.

Consequently, the actual boiler condition cannot be known. This is demonstrated by the difference in ultrasonic tubewall thickness measurements between the two low NO_x intervals. There was definite wastage during the first period, but no wastage during the last six months of reduced NO_x operation. The reasons for this difference are not clear. Possible explanations include:

- Excess air operation of the lower two burner levels
- Change in fuel characteristics
- Improvements in boiler operation due to repair of previously inoperative wall blowers

- Improved combustion system performance (prior to the last six month period scheduled maintenance had been performed on the burners and mills)

- The unit had been converted to balanced draft operation between the two reduced NO_x intervals.

However, it is quite clear that significant tube wastage did occur in the burner zone (test panels 3, 4, 5, 6) during the first reduced NO_x period.

3.0 TEST PANEL ANALYSES

All test panels were covered with plastic sheeting, crated and shipped to Foster Wheeler Development Corp. for analysis. The following results were obtained:

3.1 Chemical Analyses

Selected quantitative and qualitative spectrochemical analyses were performed on deposits removed from the outside surfaces of tubes in selected test panels. The results of the chemical analyses, which are shown in Table 1, indicate that the sulfur contents in the deposits ranged from 1 to 7%. A correlation between chemical composition of corrosion product and severity of attack was not definitive due to the loosely adherent nature of the deposits which were largely fragmented and interspersed as a result of the various panel handling operations.

Although considerable care was taken in removing the panels from the boiler, packing and shipping them, it was not possible to prevent the scale from flaking off the surface. As a consequence only the chemical composition of the overall panel could be determined. Corrosion products could not be traced to individual tubes. This is not of great significance since, when the tube wastage occurred, it did so over the entire panel; the tube-to-tube variations were generally not large.

3.2 Visual/Macroscopic Examination

Visual examination of the outside surfaces of the tube panels showed the tubes contained varying amounts of loosely adherent and fragmented overlying deposits, which exhibited various hues of white, yellow, tan, brown, red and black. Photographs illustrating the as-received appearances of the first set of test panels submitted are shown in

Figures 1-4, while the appearances of the second set of panels are shown in Figures 5-8, inclusive. It will be noted that the first set, Panel No. 4 tubes, contained the heaviest concentrations of deposits. (This panel also exhibited highest tube wall losses as determined by ultrasonic measurements.)

The grit blasted appearances of underlying fireside surfaces of tube sections cut at various locations shown in Figures 1-8 are shown in Figures 9-18, inclusive. Photomacrographs illustrating the transverse cross sectional appearances of tubes removed from selected test panels are shown in Figures 19-28.

3.3 Microscopic Examination

Intensive microscopic examinations were made of all test sections on the fireside and cold side outside surfaces as well as on the tube inside surfaces.

The examination showed that although a number of tubes were from different heats of material, they exhibited normalized microstructures characteristic of as-received tubing with no evidence of overheating occurring as a consequence of unit operation.

The microscopic examination confirmed that the odd-numbered tubes in the initial test panels are carbon steel and the even-numbered tubes are 1/2Cr-1/2Mo material. The 3 original boiler tubes and both tubes in the replacement panels are carbon steel. A decarburized layer of slightly less than 1 mil produced during tube manufacture exists on the cold faces of the initial test panel tubes and original boiler tubes. The zone is absent in both replacement panel tubes.

Representative photomicrographs illustrating the transverse cross sectional appearances of specimens removed from inside and outside surfaces of the fireside and cold side tube faces are shown in Figures 29-36, inclusive.

3.4 Hardness Measurements

Hardness measurements were also made around the circumference of the 3/8 in. wide ring sections illustrated in Figures 19-28. The results show that uniform hardnesses exist around the tube circumferences and that no significant differences in hardness values exist between the fireside and diametrically opposite tube faces.

4.0 TUBE WALL THICKNESS MEASUREMENTS

Post test tube wall thicknesses were determined by ultrasonic and micrometer measurements.

The ultrasonic tube wall measurements were made on all tubes in the 16 test panels using a calibrated Branson Caliper CL204 instrument. The measurements were made on the fireside and diametrically opposite side surfaces at 3-in. and 6-in. intervals along the lengths of the tubes which were vapor-blast-cleaned of all occluded corrosion products.

The ultrasonic measurements were correlated with pretest measurements to determine the magnitude of tube wall losses occurring as a consequence of the test exposures. The results, which are summarized in Table 2 and detailed in Tables 3-10, inclusive, indicate that the fireside surfaces suffered loss of material as compared to the diametrically opposite tube surfaces. Tubes in Initial Test Panel Nos. 1, 2, 7 and 8, and tubes in all 8 replacement panels showed no significant tube wall reductions; tubes in Panel 5 showed slight tube wall losses; and tubes in Panel Nos. 6, 3 and 4 showed increasing tube wall losses generally ranging from 7 to 21 mils with one questionable point (panel 4, tube 5 on Table No. 2) at 50 mils.

The micrometer measurements were made on 3/8-in. ring sections removed from selected tubes shown in Figures 1-8. The locations and values of the measurements are shown in Figures 19-28, and an averaged compilation of the values is summarized in Table 11 along with tube OD and hardness measurements.

5.0 DISCUSSION OF LABORATORY EVALUATION

The severity of corrosion processes occurring on tubes as a consequence of furnace exposure was determined primarily by differences in pre and post-test tube wall thicknesses recorded by ultrasonic measurement. The measurement technique provided the best means for assessing the magnitude of wastage processes occurring as a consequence of panel exposure and location within the furnace and provided the best insight concerning the relative corrosivity of the test environments during the exposure periods.

In summary, the ultrasonic tube wall measurements, which are summarized in Table 2, show the fireside tube surfaces exhibit greater attack than the diametrically opposite surfaces; that the highest attack occurs in tubes located in Initial Test Panel Nos. 3, 4, and 6; that only slight attack occurs in tubes located in Initial Test Panel No. 5; that no significant attack occurs in tubes located in Initial Test Panel Nos. 1, 2, 7 and 8. The measurement also showed that tubes in the replacement panels, which were exposed for approximately 6 months, showed no significant evidence of corrosive attack.

The slightness of the differences in tube wall losses incurred by tubes exposed for the 23-month test period over the 17-month test period and the absence of losses in tubes in all 8 replacement panels, suggests that corrosion processes were ameliorated shortly after the replacement test panels were installed. The corrosion processes may have been ameliorated as a result of a decreased number of unit startup and shutdown operations, improved efficiency of the soot blowing operations in removing accumulated deposits from the tubing surfaces, and/or changes in flue gas composition.

The post-test ultrasonic tube wall measurements for Tube Nos. 1 and 5 in Initial Test Panel No. 4 are anomalous in that while both tubes were in the same test panel, Tube No. 1 showed an increase (6 mils) in wall thickness, while Tube No. 5 showed a significant decrease in tube wall thickness (50 mils).

The measurements were confirmed by ultrasonic and micrometer methods made on transverse ring sections cut along the tube lengths. While the cause of the anomaly has not been established, it may be due to operator or instrument error occurring in initial test measurements. The disparity in values exceeds instrument reproducibility, which varies from several mils or more depending upon point-to-point tube surface conditions.

The results of the hardness measurements and microstructural examinations made on the outside and inside surfaces of the tubing sections showed no significant differences in tube material hardnesses or microstructures. The microstructure of the material indicated that while the selected sections of tubing came from different heats of carbon and 1/2Cr-1/2Mo materials, they exhibited normalized microstructures characteristic of as-received tubing and were not subjected to overheating due to unit operation.

6.0 CONCLUSION AND RECOMMENDATIONS

On the basis of the laboratory examination described herein and a review of the boiler's test conditions, the following conclusions have been made:

1. Ultrasonic tube wall thickness measurements indicate corrosive attack is confined primarily to the outside fireside surfaces of tubes located in Initial Test Panel Nos. 3, 4, and 6 with slight attack occurring on tubes in Panel No. 5. Panels 3, 4, 5 are located in the boiler left sidewall on the same level as the center burner row. Panel 4 is at the center of the sidewall while panel 5 is near the front firing wall. The relatively low metal loss on Panel 5 may be due to a different atmosphere, over the long term, as compared to Panels 3 and 4. This could be a result of secondary air flow being unbalanced between the front and rear firing walls, different pulverizer loadings, unbalanced registers or mills out of service.

   It should be noted that, during the initial reduced NO_x operating period, each pulverizer was removed from service for planned replacement of grinding elements and other maintenance. Since registers of the out of service burners remained open, at Exxon's request, that side of the lower furnace was at oxidizing conditions. However, the length of time each Panel was in a reducing atmosphere could not be determined. The precise reason for the difference in corrosion rates between Panels 3 and 5 is not clear.

   Panels 4 and 6, being located in the region of the sidewall which has been historically most susceptible to wastage, did show the greatest metal loss. Corrosion in Panel 6 was less severe, probably because the top burner level was always operated at high excess air.

2. No significant tube wall losses occur on tubes located in Initial Test Panel Nos. 1, 2, 7, and 8 after exposure test periods of 17 and 23 months. Panels 1 and 2 were located in the left sidewall near the hopper slope. This is a cool region and has generally not been an area of severe corrosion unless there is simultaneously a severe slagging problem. Panels 7 and 8 were located well above (27') the top burner level on the left and right sidewalls respectively. This area should always be at oxidizing conditions and generally does not suffer wastage.

3. No significant tube wall losses occur on tubes located in all 8 Replacement Test Panels after exposure test period of 6 months.

   The study indicates that the corrosive environment conditions may have been ameliorated during the last period of operation.

   a. Differences in tube wall losses incurred on tubes in Initial Test Panel Nos. 3, 4, and 6 during the 17 and 23 month periods of operation are minimal.

   b. Corrosive attack occurring on replacement panel tubes is insignificant after 6 months of operation.

   This result was not expected since the boiler was supposed to be operated in the same manner as during the initial reduced NO_x period. A satisfactory explanation has not been arrived at within the confines of the test and operating data obtained by Exxon.

4. There are no significant differences in the corrosion behavior of low carbon (SA210A) and 1/2Cr-1/2Mo (SA213T2) tubing materials.

5. A definitive correlation between the severity of corrosive attack and the chemical compositions of overlying deposits was not established.
    a. The sulfur contents of occluded deposits ranged from 1 to 7%.
    b. The highest sulfur content (7%) was found in deposits removed from Panel No. 4, which suffered the highest rate of attack.

6. The tubing was not overheated during unit operation.
    a. Hardness values around tube circumferences are fairly uniform and representative of as-received tubing.
    b. Tubing material is devoid of microstructural changes and exhibits normalized microstructres characteristic of as-received tubing.

This demonstrates that the observed corrosion was caused by the fireside environment rather than any waterside upset.

The results confirm that when furnace staging is used for reducing NO_x in a high heat release rate boiler, firing high sulfur bituminous coal, there is a significant increase in corrosion rate within the firing zone. However, when staging is minimized, (i.e. oxidizing conditions, as may have been the case after the first six months of low-NO_x operation), there is a potential for minimal corrosion. It has been Foster Wheeler Energy Corp.'s opinion that staging should not be used on such pre-NSPS boilers for NO_x control. Rather, low NO_x burners should be retrofitted to boilers which may be required to reduce NO_x emissions. A properly designed low NO_x burner will allow the operators full flexibility of unit operation with no degradation in boiler performance or efficiency. Burners of this type have been field-demonstrated and offered commercially by Foster Wheeler for some years.

Staging, by itself, is not capable of yielding large NO_x reductions without resorting to large quantities of overfire air. Reducing burner stoichiometry to 95-100% at full load and design excess air will only yield typical NO_x reductions of 30-40% in pre-NSPS boilers. However, as these corrosion results have confirmed, significant corrosion rates can occur as a result of staging.

In comparison, low NO_x burners can provide a minimum of 40% NO_x reduction at normal burner stoichiometry: burner excess air equal to boiler excess air. Tube wastage, even with high sulfur coal, should be minimal.

TABLE 1.

Chemical Analyses of Corrosion Products

Panel No./Set No.	3/1	3/2	4/1	4/2	5/1	5/2	6/1	6/2	7/1	8/2
Exposure Time, Mos.	17	23	17	23	17	23	17	23	23	17
Element										
Na	L	L	L	L	L	L	L	L	L	L
Mg	L	T	T	L	L	L	L	L	L	L
Al	M	L	L	M	L	L	L	M	M	M
Si	M	L	L	M	M	M	M	M	M	M
K	L	L	L	L	L	L	L	L	L	L
Ca	L	L	L	L	L	M	L	L	L	L
Ti	L	L	L	L	T	L	L	L	L	L
V	T	T	T	T	T	T	T	T	T	T
Cr	T	L	T	T	T	T	T	T	T	T
Mn	L	L	L	L	L	L	L	L	L	L
Fe	H	H	H	H	H	H	H	H	H	H
Ni	T	T	T	T	T	T	T	T	T	T
Cu	L	T	L	L	T	L	L	L	T	L
Zn	L	L	L	L	L	L	L	L	L	L
Mo	L	L	L	L	L	L	L	L	L	L
Ag	FT	FT	FT	FT	FT	FT	FT	FT	FT	FT
Sn	T	T	T	T	T	T	T	T	T	T
Pb	L	L	L	L	L	L	L	L	L	L
Sulfur, %	6.38	1.27	7.04	3.77	3.67	2.16	3.39	4.26	2.58	5.68

CODE

ND - Not Detected
VVFT <.0001%
VFT .0001%-.001%
FT - .001% - .01%
T - .01 - .1%
L - .1 - 1%
M - 1% - 10%
H - >10%

TABLE 2

Summary of Ultrasonically Measured Tube Wall Thickness Changes Occuring as a Result of Test Exposure
(Averaged Values, in mils)

Panel No.	Side(1)	TUBE NO.						
		1	2	3	4	5	RP-1	RP-2
1	HS	- 4.5	- 1.6	- 1.5	+ .9	- 1.4	+ 1.5	+ 1.1
	CS	- 1.5	- .4	- 2.1	+ 1.0	- .9	+ .3	- 1.8
	TM	23	23	23	17	17	6	6
2	HS	+ .47	+ .59	- 2.3	- 2.4	- 1.6	+ 1.2	+ 1.6
	CS	+ .50	+ .63	- 1.1	- 1.5	- 1.2	+ 1.2	- .5
	TM	17	17	23	23	23	6	6
3	HS	-15.3	-12.9	-11.1	-14.6	-13.2	+ 1.1	+ 2.0
	CS	- 1.4	+ .42	- .3	+ .3	- 2.3	+ 1.8	+ .8
	TM	17	17	23	23	23	6	6
4	HS	+ 6.6	-15.8	-20.9	-20.1	-49.9	+ .9	+ 2.0
	CS	+ .4	+ .1	- 1.3	+ 1.4	+ .1	+ 3.0	+ 1.7
	TM	23	23	23	17	17	6	6
5	HS	- 1.9	- .3	- 3.6	- 2.3	- 3.8	+ 2.0	+ .9
	CS	+ .7	+ .1	- .3	- 1.9	- 1.6	0	+13.4
	TM	17	17	23	23	23	6	6
6	HS	-10.7	- 9.3	- 8.5	- 7.5	- 7.1	+ 2.0	+ 2.8
	CS	--	--	- .5	- 2.1	- 3.0	+ 2.9	+ 2.8
	TM	23	23	23	17	17	6	6
7	HS	- .7	- 1.8	- 2.1	- .3	- .4	+ 1.8	+ ..4
	CS	+ 1.0	+ .6	- .7	+ 1.7	+ 1.3	+ 2.6	+ 2.8
	TM	23	23	23	17	17	6	6
8	HS	+ .6	0	- 1.2	- .5	+ .4	+ 1.9	+ 1.9
	CS	+ .8	+ 1.9	+ .6	+ 1.8	+ 2.8	+ 1.4	+ .9
	TM	17	17	23	23	23	6	6

(1) HS = Hot Side
CS = Cold Side
TM = Exposure Time in months

Tube Material: ITP 1, 3, 5 - SA210
ITP 2, 4 - SA213T2
RP1 }
RP2 } - SA210

TABLE 3

Ultrasonic Tube Wall Thickness Measurements (in mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 1																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
1	23			HS	B	306	305	306	306	306	306	305	305	305	305	305	306	305	305	305	305	305				
	23			HS	A	302	304	304	299	300	299	301	299	298	299	296	300	300	303	305	303	302				
	23			HS	Δ	-4	-1	-2	-7	-6	-7	-4	-6	-7	-6	-9	-6	-5	-2	0	-2	-3				
	23			CS	B		301		301		301		302		302		302		301		301					-4.5
	23			CS	A		299		299		301		300		300		300		300		300					
				CS	Δ		-2		-2		0		-2		-2		-2		-1		-1					
																										-1.5
2	23			HS	B	317	317	317	317	317	316	317	316	316	316	316	316	316	316	316	316	316				
	23			HS	A	314	316	312	311	313	315	315	315	313	311	317	319	315	316	316	316	316				
	23			HS	Δ	-3	-1	-5	-6	-4	-1	-2	-1	-3	-5	+1	+3	-1	0	0	0	0				
	23			CS	B		310		309		309		310		310		311		310		310					-1.6
	23			CS	A		310		310		310		310		310		308		309		309					
	23			CS	Δ		0		+1		+1		0		0		-3		-1		-1					
																										-.4
3	23			HS	B	287	288	288	287	288	287	288	288	288	289	290	289	289	290	289	290	290				
	23			HS	A	290	288	283	287	285	285	285	287	292	290	286	290	288	284	286	286	287				
	23			HS	Δ	+3	0	-5	0	-3	-2	-3	-1	+4	+1	-4	+1	-1	-6	-3	-4	-3				
	23			CS	B		317		317		317		317		316		316		317		315					-1.5
	23			CS	A		313		316		313		313		316		316		315		313					
	23			CS	Δ		-4		-1		-4		-4		0		0		-2		-2					
																										-2.1
4	17			HS	B	317	317	316	316	317	317	317	317	318	317	317	317	317	316	316	316	316				
	17			HS	A	318	318	319	318	319	321	320	318	318	316	319	316	316	316	318	316	313				
	17			HS	Δ	+1	+1	+3	+2	+2	+4	+3	+1	0	-1	+2	-1	-1	0	+2	0	-3				
	17			CS	B		309		309		310		309		309		309		309		310					+ .9
	17			CS	A		311		311		310		310		309		310		310		311					
	17			CS	Δ		+2		+2		0		+1		0		+1		+1		+1					
																										+1.0
5	17			HS	B	302	302	304	303	304	302	303	302	302	301	302	301	300	299	299	299	299				
	17			HS	A	303	303	304	304	301	300	299	298	299		298	297	297	299	299	299	299				
	17			HS	Δ	+1	+1	0	+1	-3	-2	-4	-4	-3		-4	-4	-3	0	0	0	0				
	17			CS	B		302		304		305		305		306		306		307		306					-1.4
	17			CS	A		304		306		304		306		306		308		309		304					
	17			CS	Δ		+2		+2		-1		+1		0		+2		+2		-2					
																										- .9

TABLE 3 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure	Micro	Tube Side	Before After	PANEL NO. 1																				
						3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
RP-1	6			HS	B		315		313		314		314		313		315		315		316		315		316	
	6			HS	A	314	314	312	314	315	316	314	315	316	314	316	316	317	318	317	318	317	318	320	318	
	6			HS	Δ		-1		+1		+2		+1		+1		+1		+3		+2		+3		+2	+1.5
	6			CS	B		316		317		315		315		313		315		311		312		310		309	
	6			CS	A		314		314		316		314		315		315		313		313		312		310	
	6			CS	Δ		-2		-3		+1		-1		+2		0		+2		+1		+2		+1	+0.3
RP-2	6			HS	B		318		316		318		317		317		316		316		315		312		311	
	6			HS	A	317	316	318	317	319	319	319	318	319	317	317	317	318	317	317	318	316	314	313	314	
	6			HS	Δ		-2		+1		+1		+1		0		+1		+1		+3		+2		+3	+1.1
	6			CS	B		313		313		314		314		313		315		312		312		317		318	
	6			CS	A		312		311		309		311		311		313		313		312		314		317	
				CS	Δ		-1		-2		-5		-3		-2		-2		+1		0		-3		-1	-1.8

TABLE 4

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 2																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
1	17			HS	B	295	294	294	293	296	297	297	299	298	297	298	297	300	300	301	300	300				
	17			HS	A	296	295	296	296	299	300	298	296	295	299	299	297	298	300	299	301	300				
	17			HS	Δ	+1	+1	+2	+3	+3	+3	+1	-3	-3	+2	+1	0	-2	0	-2	+1	0				+ .47
	17			CS	B		313		313		310		309		311		311		307		308					
	17			CS	A		313		315		311		310		311		311		308		307					
	17			CS	Δ		0		+2		+1		+1		0		0		+1		-1					+.50
2	17			HS	B	317	317	317	317	317	317	317	317	317	317	317	317	315	315	316	316	315				
	17			HS	A	315	316	316	316	319	320	317	317	320	318	319	316	317	317	315	315	318				
	17			HS	Δ	-2	-1	-1	-1	+2	+3	0	0	+3	+1	+2	-1	+2	+2	-1	-1	+3				+.59
	17			CS	B		312		312		311		311		311		312		313		313					
	17			CS	A		312		312		311		311		311		314		314		315					
	17			CS	Δ		0		0		0		0		0		+2		+1		+2					+.63
3	23			HS	B	285	285	285	286	287	289	289	289	286	290	291	291	291	292	293	293	293				
	23			HS	A	281	281	282	284	285	286	288	286	284	289	289	289	292	290	289	291	288				
	23			HS	Δ	-4	-4	-3	-2	-2	-3	-1	-3	-2	-1	-2	-2	+1	-2	-4	-2	-5				-2.3
	23			CS	B		321		321		318		316		316		314		313		313					
	23			CS	A		321		318		318		316		313		313		312		312					
	23			CS	Δ		0		-3		0		0		-3		-1		-1		-1					-1.1
4	23			HS	B	314	313	313	314	315	315	315	316	317	317	317	317	318	318	319	319	319				
	23			HS	A	310	310	309	309	311	313	313	313	315	316	318	316	318	316	316	317	315				
	23			HS	Δ	-4	-3	-4	-5	-4	-2	-2	-3	-2	-1	+1	-1	0	-2	-3	-2	-4				-2.4
	23			CS	B		313		314		313		311		311		311		310		309					
	23			CS	A		313		313		309		310		310		309		308		308					
	23			CS	Δ		0		-1		-4		-1		-1		-2		-2		-1					-1.5
5	23			HS	B	289	290	289	290	290	288	288	288	287	288	288	287	286	287	286	286	287				
	23			HS	A	287	284	288	286	286	286	287	285	288	288	288	288	286	286	284	284	285				
	23			HS	Δ	-2	-6	-1	-4	-4	-2	-1	-3	+1	0	0	+1	0	-1	-2	-2	-2				-1.6
	23			CS	B		316		317		319		320		320		320		320		320					
	23			CS	A		314		316		317		318		318		319		317		319					
	23			CS	Δ		-2		-1		-2		-2		-2		-1		-3		-1					-1.8

TABLE 4 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 2																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
RP-1	6			HS	B		317		317		316		318		315		317		317		319		315		316	
	6			HS	A	318	318	320	318	318	319	319	319	318	317	317	318	319	318	318	319	318	316	318	317	
	6			HS	Δ		+1		+1		+3		+1		+2		+1		+1		0		+1		+1	+1.2
	6			CS	B		305		307		307		307		307		309		309		309		309		309	
	6			CS	A		309		305		309		308		309		311		310		309		310		310	
	6			CS	Δ		+4		-2		+2		+1		+2		+2		+1		0		+1		+1	+1.2
RP-2	6			HS	B·		323		326		325		326		327		328		329		330		331		330	
	6			HS	A	329	325	327	326	326	326	328	328	328	329	330	330	331	331	331	333	333	332	332	331	
	6			HS	Δ		+2		0		+1		+2		+2		+2		+2		+3		+1		+1	+1.6
	6			CS	B		303		303		303		303		300		302		300		298		298		299	
	6			CS	A		304		304		303		302		301		300		299		298		294		299	
	6			CS	Δ		+1		+1		0		-1		+1		-2		-1		0		-4		0	- .5

TABLE 5

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 3																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
1	17			HS	B	317	316	316	315	315	313	314	314	313	313	312	311	309	309	309	310	310				
	17		294	HS	A	307	304	300	303	304	294	299	300	297	290	293	299	296	291	296						
	17			HS	Δ	-17	-12	-16	-12	-11	-19	-15	-14	-16	-23	-19	-12	-13	-18	-13						-15.
	17			CS	B		291		293		295		295		295		296		298		296					
	17		295	CS	A		292		292		294		293		294		294		294							
	17			CS	Δ		+1		-1		-1		-2		-1		-2		-4							-1.4
2	17			HS	B	319	319	319	320	320	319	318	319	319	319	318	319	319	318	318	318	318				
	17		305	HS	A	308	308	312	308	307	307	309	301	304	300	304	304	308	306	303						
	17			HS	Δ	-11	-11	-7	-12	-13	-12	-9	-18	-15	-19	-14	-15	-11	-12	-15						-12.
	17			CS	B		308		307		309		308		309		308		308		309					
	17		307	CS	A		308		308		309		308		309		308		310							
	17			CS	Δ		0		+1		0		0		0		0		+2							+.42
3	23			HS	B	308	307	306	308	307	305	307	305	304	305	303	305	305	304	305	303	302				
	23		293	HS	A	293	294	294	287	296	294	298	288	294	289	300	295	299	302							
	23			HS	Δ	-15	-13	-12	-21	-11	-11	-9	-17	-10	-16	-3	-10	-6	-2							-11.1
	23			CS	B		297		296		299		300		299		299		300		302					
	23		293	CS	A		300		300		297		297		299		297		298							
	23			CS	Δ		+3		+4		-2		-3		0		-2		-2							- .3
4	23			HS	B	305	304	304	304	304	304	304	304	304	303	303	302	302	302	302	301	301				
	23		288	HS	A	285	287	287	290	294	289	289	291	290	289	287	287	292	285							
	23			HS	Δ	-20	-17	-17	-14	-8	-15	-15	-13	-14	-14	-16	-15	-10	-17							-14.6
	23			CS	B		322		323		324		324		324		325		326		325					
	23		319	CS	A		324		325		325		325		324		324		323							
	23			CS	Δ		+2		+2		+1		+1		0		-1		-3							+ .3
5	23			HS	B	300	297	298	297	297	297	296	297	297	295	295	294	295	294	294	294	294				
	23		--	HS	A	279	284	288	284	276	276	279	278	285	289	295	283	283	285							
	23			HS	Δ	-21	-13	-10	-13	-21	-21	-17	-19	-12	-6	0	-11	-12	-9							-13.2
	23			CS	B		308		309		309		308		310		310		311		310					
	23		--	CS	A		308		307		309		309		305		306		305							
	23			CS	Δ		0		-2		0		+1		-5		-4		-6							-2.3

TABLE 5 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 3																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
RP-1	6			HS	B		313		315		314		314		316		316		314		315		316		313	
	6		310	HS	A	313	315	316	315	317	316	316	316	317	317	316	317	317	315	314	315	316	317			
	6			HS	Δ		+2		0		+2		+2		+1		+1		+1		0		+1			+1.1
	6			CS	B		309		309		311		310		309		306		309		311		308		311	
	6		306	CS	A		311		310		313		312		310		310		311		312		309			
	6			CS	Δ		+2		+1		+2		+2		+1		+4		+2		+1		+1			+1.8
RP-2	6			HS	B·		311		312		311		311		311		312		311		312		311		308	
	6		308	HS	A	314	313	315	314	315	314	313	314	314	313	313	313	313	312	311	314	312	313			
	6			HS	Δ		+2		+2		+3		+3		+2		+1		+1		+2		+2			+2.0
	6			CS	B		311		313		312		313		313		312		313		312		314		312	
	6		309	CS	A		315		312		312		313		315		314		314		312		313			
	6			CS	Δ		+4		-1		0		0		+2		+2		+1		0		-1			+ .8

TABLE 6

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 4																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
1	23			HS	B	294	294	296	292	294	294	291	293	292	291	294	291	289	293	289	292	295				
	23		288	HS	A	296	296	301	300	303	301	304	296	302	303	291	298	300								
	23			HS	Δ	+2	+2	+5	+8	+9	+7	+13	+3	+10	+12	-3	+7	+11								+6.6
	23			CS	B		285		285		284		283		284		285		285		285					
	23		295	CS	A		286		283		286		285		283		285		286							
	23			CS	Δ		+1		-2		+2		+2		-1		0		+1							+ .4
2	23			HS	B	314	313	312	312	312	312	314	314	315	315	314	314	314	314	314	315	315				
	23		289	HS	A	301	297	300	293	296	300	302	297	299	302	292	294	296								
	23			HS	Δ	-13	-16	-12	-19	-16	-12	-12	-17	-16	-13	-22	-20	-18								-15.8
	23			CS	B		311		311		310		310		310		310		309		310					
	23		307	CS	A		310		311		311		310		311		309		310							
	23			CS	Δ		-1		0		+1		0		+1		-1		+1							+ .1
3	23			HS	B	309	308	308	307	308	309	307	306	305	306	305	304	305	305	305	306	306				
	23		--	HS	A	291	291	285	285	291	288	280	288	292	281	283	280	282	283							
	23			HS	Δ	-18	-17	-23	-22	-18	-21	-27	-18	-13	-25	-22	-24	-23	-22							-20.9
	23			CS	B		299		300		300		300		301		302		301		302					
	23		--	CS	A		300		299		297		301		299		299		299							
	23			CS	Δ		+1		-1		-3		+1		-2		-3		-2							-1.3
4	17			HS	B	317	316	316	316	316	317	318	317	318	317	317	317	318	318	318	318	318				
	17		312	HS	A	299	295	293	298	298	300	301	297	298	293	295	297	300	296	295						
	17			HS	Δ	-18	-21	-23	-18	-18	-17	-17	-20	-20	-24	-22	-20	-18	-22	-23						-20.1
	17			CS	B		314		315		314		313		313		314		313		312					
	17		312	CS	A		315		316		316		315		314		316		314							
	17			CS	Δ		+1		+1		+2		+2		+1		+2		+1							+1.4
5	17			HS	B	323	322	323	322	322	323	322	323	322	323	322	322	321	322	321	322	322				
	17		297	HS	A	272	278	271	276	279	275	271	276	268	270	270	270	269	272	268						
	17			HS	Δ	-51	-44	-52	-46	-43	-48	-51	-47	-54	-53	-52	-52	-52	-50	-53						-49.9
	17			CS	B		310		312		310		311		314		314		311		312					
	17		299	CS	A		311		312		310		312		314		313		311							
				CS	Δ		+1		0		0		+1		0		-1		0							+ .1

TABLE 6 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 4																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
RP-1	6			HS	B		314		313		313		313		311		310		309		306		302			
	6		301	HS	A	316	317	315	316	316	315	312	315	309	308	308	311	310	310	308	304	303	303		303	
	6			HS	Δ		+3		+3		+2		+2		-3		+1		+1		-2		+1			+ .9
	6			CS	B		311		312		312		313		314		317		319		320		324			
	6		321	CS	A		313		314		316		317		318		320		321		324		326		324	
	6			CS	Δ		+2		+2		+4		+4		+4		+3		+2		+4		+2			+3.0
RP-2	6			HS	B		325		323		320		324		324		320		320		321		320			
	6		311	HS	A	326	327	325	325	324	323	323	326	327	325	324	323	324	322	320	323	320	321		318	
	6			HS	Δ		+2		+2		+3		+2		+1		+3		+2		+2		+1			+2.0
	6			CS	B		301		302		303		302		303		305		304		305		308			
	6		305	CS	A		302		304		305		303		304		306		307		308		309		309	
	6			CS	Δ		+1		+2		+2		+1		+1		+1		+3		+3		+1			+1.7

TABLE 7

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 5																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
1	17			HS	B	314	314	312	312	312	313	312	312	312	311	313	312	312	312	311	312	310				
	17		303	HS	A	--	--	312	313	312	312	310	310	306	308	311	309	310	311	308	309	308				
	17			HS	Δ			0	+1	0	-1	-2	-2	-6	-3	-2	-3	-2	-1	-3	-3	-2				-1.9
	17			CS	B		292		293		294		295		295		295		295		296					
	17		292	CS	A				293		294		295		296		296		297		297					
	17			CS	Δ				0		0		0		+1		+1		+2		+1					+ .7
2	17			HS	B	323	323	322	321	321	321	321	321	320	321	320	321	320	319	318	318	318				
	17		316	HS	A			322	323	322	321	321	321	319	317	320	319	320	319	318	318	318				
	17			HS	Δ			0	+2	+1	0	0	0	-1	-4	0	-2	0	0	0	0	0				- .3
	17			CS	B		305		305		305		306		306		307		307		310					
	17		305	CS	A				304		306		306		306		306		308		309					
	17			CS	Δ				-1		+1		0		0		-1		+1		-1					- .1
3	23			HS	B	294	294	296	295	296	297	296	296	294	293	294	295	295	296	294	295	293				
	23		288	HS	A	291	289	291	295	292	295	294	293	288	288	291	292	293	289							
	23			HS	Δ	-3	-5	-5	0	-4	-2	-2	-3	-6	-5	-3	-3	-2	-7	--	--	--				-3.6
	23			CS	B		313		311		309		311		313		312		311		313					
	23		306	CS	A		311		311		310		311		313		311		311							
	23			CS	Δ		-2		0		+1		0		0		-1		0							- .3
4	23			HS	B	316	318	317	317	317	317	317	317	317	317	317	317	317	317	315	315	314				
	23		308	HS	A	314	316	316	314	315	317	316	314	316	316	315	310	314	313							
	23			HS	Δ	-2	-2	-1	-3	-2	0	-1	-3	-1	-1	-2	-7	-3	-4							-2.3
	23			CS	B		309		309		310		310		310		310		310		312					
	23		306	CS	A		307		308		309		309		309		304		309							
	23			CS	Δ		-2		-1		-1		-1		-1		-6		-1							-1.9
5	23			HS	B	308	308	308	309	310	310	311	311	311	313	313	314	313	313	313	313	313				
	23		--	HS	A	306	304	305	306	306	308	307	308	308	306	307	310	307	311							
	23			HS	Δ	-2	-4	-3	-3	-4	-2	-4	-3	-3	-7	-6	-4	-6	-2							-3.8
	23			CS	B		298		296		295		292		292		290		291		291					
	23		--	CS	A		295		295		291		291		292		288		291							
	23			CS	Δ		-3		-1		-4		-1		0		-2		0							-1.6

TABLE 7 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 5																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
RP-1																										
				HS	B		321		322		322		320		320		320		317		317		313		315	
			313	HS	A	324	323	323	324	323	325	324	323	321	321	320	320	320	320	318	319	318	315			
				HS	Δ		+2		+2		+3		+3		+1		0		+3		+2		+2		---	+2.0
				CS	B		311		311		310		309		309		307		310		305		304		306	
			310	CS	A		307		306		304		306		309		310		310		312		312			
				CS	Δ		-4		-5		-6		-3		0		+3		0		+7		+8			0
RP-2																										
				HS	B		304		303		303		302		303		302		301		303		304		304	
			300	HS	A	305	306	305	304	303	303	302	303	304	304	304	303	302	300	304	305	304	303			
				HS	Δ		+2		+1		0		+1		+1		+1		+1		+2		-1			+ .9
				CS	B		304		307		307		309		307		314		316		316		315		316	
			315	CS	A		324		324		323		323		325		325		324		323		323			
				CS	Δ		+20		+17		+16		+17		+18		+11		+8		+7		+8			+13.4

TABLE 8

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	P A N E L N O. 6																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
1	23	31.32		HS	B	293	292	292	293	294	294	293	294	295	296	295	293	294	295	296	295	295				
	23		273	HS	A	291	284	287	289	281	284	284	278	282	284	281	282	283	281	280						
	23			HS	Δ	-2	-8	-5	-4	-13	-10	-9	-16	-13	-12	-14	-11	-11	-14	-19						-10.7
	23	31.32		CS	B		315		314		314		312		312		313		310		312					
	23		308	CS	A		--		--		--		--		--		--		--		--					
				CS	Δ		--		--		--		--		--		--		--		--					--
2	23	33.34		HS	B	313	314	314	312	312	312	312	314	314	315	314	313	313	312	313	312	312				
	23		298	HS	A	303	306	306	301	304	307	306	305	308	305	304	301	300	302	300						
	23			HS	Δ	-10	-8	-8	-11	-8	-5	-6	-9	-6	-10	-10	-12	-13	-10	-13						-9.3
	23	33.34		CS	B		316		318		318		316		315		318		318		318					
	23		312	CS	A		--		--		--		--		--		--		--		--					
	23			CS	Δ		--		--		--		--		--		--		--		--					--
3	23			HS	B	309	307	308	308	307	307	306	306	306	306	305	305	307	307	307	307	307				
	23		--	HS	A	296	293	300	301	300	299	297	296	292	298	293	301	297	304	301						
	23			HS	Δ	-13	-14	-8	-7	-7	-8	-9	-10	-9	-8	-12	-4	-10	-3	-6						-8.5
	23			CS	B		298		299		300		300		300		300		299		299					
	23		--	CS	A		298		300		299		299		299		299									
	23			CS	Δ		0		+1		-1		-1		-1		-1									- .5
4	17			HS	B	321	320	320	320	321	321	321	320	320	320	321	321	321	322	322	321	321				
	17		310	HS	A	314	313	314	312	315	316	314	313	312	312	316	312	311	312	313						
	17			HS	Δ	-7	-7	-6	-8	-6	-5	-7	-7	-8	-8	-5	-9	-10	-10	-9						-7.5
	17			CS	B		311		310		309		309		309		308		308		308					
	17		307	CS	A		309		304		307		306		308		308		307							
	17			CS	Δ		-2		-6		-2		-3		-1		0		-1							-2.1
5	17			HS	B	300	300	301	301	300	300	300	300	300	298	298	298	296	295	295	294	292				
	17		289	HS	A	290	293	291	291	295	292	292	295	292	290	293	291	291	290	290						
	17			HS	Δ	-10	-7	-10	-10	-5	-8	-8	-5	-8	-8	-6	-7	-5	-5	-5						-7.1
	17			CS	B	307		307		307		307		310		310		312		312						
	17		306	CS	A	304		303		300		306		309		307		310								
	17			CS	Δ	-3		-4		-7		-1		-1		-3		-2								-3.0

TABLE 8 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 6																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
RP-1	6	35,36		HS	B		307		308		310		311		313		317		313		315		313		317	
	6		310	HS	A	308	309	311	308	310	312	313	315	314	316	316	316	315	316	316	317	314	316	317		
	6			HS	Δ		+2		0		+2		+4		+3		-1		+3		+2		+3			+2.0
	6	35,36		CS	B		318		317		316		314		314		312		312		311		311		309	
	6		309	CS	A		321		320		319		318		315		316		315		315		312			
	6			CS	Δ		+3		+3		+3		+4		+1		+4		+3		+4		+1			+2.9
RP-2	6			HS	B		313		312		312		310		310		310		307		306		306		304	
	6		301	HS	A	313	316	316	316	319	315	316	313	313	309	312	311	311	311	311	311	308	309	306		
	6			HS	Δ		+3		+4		+3		+3		-1		+1		+4		+5		+3			+2.8
	6			CS	B		313		310		311		313		316		316		317		318		319		320	
	6		317	CS	A		316		312		312		317		318		319		319		323		322			
	6			CS	Δ		+3		+2		+1		+4		+2		+3		+2		+5		+3			+2.8

TABLE 9

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO. 7																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
1	23			HS	B	288	288	288	289	289	289	291	291	292	292	293	293	294	294	295	296	297				
	23		284	HS	A	286	286	285	285	288	288	288	291	291	295	294	294	295	295							
	23			HS	Δ	-2	-2	-3	-4	-1	-1	-3	0	-1	+3	+1	+1	+1	+1							- .7
	23			CS	B		318		317		316		315		314		313		311		309					
	23		309	CS	A		317		318		319		317		316		315		309							
	23			CS	Δ		-1		+1		+3		+2		+2		+2		-2							+1.0
2	23			HS	B	320	321	322	322	321	322	320	321	321	321	321	321	322	322	322	322	322				
	23		313	HS	A	320	318	319	319	319	319	319	319	319	320	320	322	318	321							
	23			HS	Δ	0	-3	-3	-3	-2	-3	-1	-2	-2	-1	-1	+1	-4	-1							-1.8
	23			CS	B		308		307		307		308		308		308		307		307					
	23		304	CS	A		308		307		310		310		309		308		306							
	23			CS	Δ		0		0		+3		+2		+1		0		-1							+ .6
3	23			HS	B	296	295	296	296	295	297	297	297	293	297	297	298	297	297	297	295	296				
	23		--	HS	A	291	290	293	295	295	298	297	297	293	294	294	295	293	293							
	23			HS	Δ	-5	-5	-3	-1	0	+1	0	0	0	-3	-3	-3	-4	-4							-2.1
	23			CS	B		311		310		309		308		308		309		309		309					
	23		--	CS	A		309		309		308		307		309		309		308							
	23			CS	Δ		-2		-1		-1		-1		+1		0		-1							- .7
4	17			HS	B	320	320	320	320	319	318	318	317	317	317	317	316	316	315	314	314	314				
	17		293	HS	A	317	318	320	317	319	318	317	316	317	317	317	318	317	316	315						
	17			HS	Δ	-3	-2	0	-3	0	0	-1	-1	0	0	0	+2	+1	+1	+1						- .3
	17			CS	B		308		308		310		310		310		311		313		314					
	17		310	CS	A		310		310		312		311		312		313		314							
	17			CS	Δ		+2		+2		+2		+1		+2		+2		+1							+1.7
5	17			HS	B	298	299	299	298	300	300	300	302	302	300	302	300	301	302	302	301	304				
	17		302	HS	A	298	299	300	299	301	299	299	301	300	300	300	299	301	302	301						
	17			HS	Δ	0	0	+1	+1	+1	-1	-1	-1	-2	0	-2	-1	0	0	-1						- .4
	17			CS	B		303		305		303		300		302		303		300		301					
	17		310	CS	A		302		305		305		303		304		304		302							
	17			CS	Δ		-1		0		+2		+3		+2		+1		+2							+1.3

TABLE 9 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO 7																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg
RP-1	6			HS	B		307		313		300		305		306		305		306		302		304		304	
	6		302	HS	A	307	308	308	308	305	308	305	307	307	308	307	306	308	308	304	305	304	306			
	6			HS	Δ		+1		-5		+8		+2		+2		+1		+2		+3		+2			+1.8
	6			CS	B		318		318		317		318		317		318		318		318		319		317	
	6		315	CS	A		319		320		319		320		321		322		322		321		320			
	6			CS	Δ		+1		+2		+2		+2		+4		+4		+4		+3		+1			+2.6
RP-2	6			HS	B		305		305		303		305		307		307		307		309		310		310	
	6		306	HS	A	306	306	306	305	305	304	306	308	308	308	309	308	310	309	307	303	310	311			
	6			HS	Δ		+1		0		+1		+3		+1		+1		+2		-6		+1			+ .4
	6			CS	B		321		322		322		319		318		318		319		316		315		315	
	6		312	CS	A		324		324		325		322		321		321		321		319		318			
	6			CS	Δ		+3		+2		+3		+3		+3		+3		+2		+3		+3			+2.8

TABLE 10

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure	Micro	Tube Side	Before After	PANEL NO 8																				Avg.
						3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	
1	17			HS	B	301	301	301	301	300	298	298	297	298	296	296	296	295	296	295	294	295				
	17			HS	A	301	302	301	301	301	300	300	298	298	296	296	297	295	297	295	295	295				
	17			HS	Δ	0	+1	0	0	+1	+2	+2	+1	0	0	0	+1	0	+1	0	+1	0				+ .6
	17			CS	B		304		304		306		308		310		309		309		310					
	17			CS	A		306		306		307		307		308		311		310		311					
	17			CS	Δ		+2		+2		+1		-1		-2		+2		+1		+1					+ .8
2	17			HS	B	302	302	302	302	302	302	301	302	302	301	302	301	301	301	302	302	301				
	17			HS	A	302	302	301	303	302	302	300	302	302	302	301	302	302	301	301	302	301				
	17			HS	Δ	0	0	-1	+1	0	0	-1	0	0	+1	-1	+1	+1	0	-1	0	0				0
	17			CS	B		325		324		324		324		324		325		325		324					
	17			CS	A		326		324		326		326		327		328		327		326					
	17			CS	Δ		+1		0		+2		+2		+3		+3		+2		+2					+1.9
3	23			HS	B	305	307	305	307	307	305	307	305	303	306	306	305	307	306	306	306	304				
	23			HS	A	303	304	302	306	306	304	305	304	302	305	305	304	305	306	305	306	304				
	23			HS	Δ	-2	-3	-3	-1	-1	-1	-2	-1	-1	-1	-1	-1	-2	0	-1	0	0				-1.2
	23			CS	B		297		295		299		298		297		298		297		297					
	23			CS	A		297		297		299		297		299		299		298		297					
	23			CS	Δ		0		+2		0		-1		+2		+1		+1		0					+ .6
4	23			HS	B	323	324	325	325	325	325	325	324	325	325	324	325	325	324	325	325	324				
	23			HS	A	323	323	324	326	325	324	326	323	325	324	322	324	325	324	323	325	324				
	23			HS	Δ	0	-1	-1	+1	0	-1	+1	-1	0	-1	-2	-1	0	0	-2	0	0				- .5
	23			CS	B		304		304		304		305		304		304		304		303					
	23			CS	A		306		304		306		305		307		306		307		305					
	23			CS	Δ		+2		0		+2		0		+3		+2		+3		+2					+1.8
5	23			HS	B	309	308	307	307	306	306	306	306	306	306	305	305	304	303	303	304	305				
	23			HS	A	310	304	304	306	307	308	307	306	309	307	305	306	304	304	304	304	306				
	23			HS	Δ	+1	-4	-3	-1	+1	+2	+1	0	+3	+1	0	+1	0	+1	+1	0	+1				+ .4
	23			CS	B		298		299		298		299		300		300		301		300					
	23			CS	A		301		300		302		301		304		303		303		303					
	23			CS	Δ		+3		+1		+4		+2		+4		+3		+2		+3					+2.8

TABLE 10 (Cont.)

Ultrasonic Tube Wall Thickness Measurements (in Mils)

Tube No. ITP	Exposure Time (Mos.)	Figure		Tube Side	Before After	PANEL NO 8																				
			Micro			3"	6"	9"	12"	15"	18"	21"	24"	27"	30"	33"	36"	39"	42"	45"	48"	51"	54"	57"	60"	Avg.
RP-1	6			HS	B		323		322		322		322		321		320		320		319		318		318	
	6			HS	A	324	325	323	324	325	324	323	323	324	322	322	322	321	322	323	321	320	320	320	321	
	6			HS	Δ		+2		+2		+2		+1		+1		+2		+2		+2		+2		+3	+1.9
	6			CS	B		302		301		302		302		302		303		304		304		305		304	
	6			CS	A		303		304		304		303		304		304		304		306		306		305	
	6			CS	Δ		+1		+3		+2		+1		+2		+1		0		+2		+1		+1	+1.4
RP-2	6			HS	B		319		318		318		318		319		319		319		318		319		316	
	6			HS	A	319	322	322	319	321	321	317	321	320	320	320	320	320	320	321	320	319	320	320	319	
	6			HS	Δ		+3		+1		+3		+3		+1		+1		+1		+2		+1		+3	+1.9
	6			CS	B		304		305		305		304		305		304		306		306		307		307	
	6			CS	A		306		307		307		305		306		300		307		308		307		309	
	6			CS	Δ		+2		+2		+2		+1		+1		-4		+1		+2		0		+2	+ .9

TABLE 11

Summary of Tube Wall, OD Micrometer Measurements and Hardness Measurements

I TUBE OD MEASUREMENTS (in inches)

Panel No.	Original Tubes		Initial Test Panel Tubes					Replacement Panel Tubes	
	No. 1	No. 2	ITP-1	ITP-2	ITP-3	ITP-4	ITP-5	RP-1	RP-2
3	3.002	3.001	2.932	2.980	2.989	2.993		2.993	3.000
4	2.993	2.982		2.988	2.973	2.992	2.962	2.992	2.986
5	2.995	2.995	2.997	2.999	2.985	2.989	--	2.997	3.001
6	3.008	3.012	2.983	2.992	--	2.982	2.987	2.991	2.982
7	2.970	2.974	3.002	2.991	--	2.990	2.990	2.985	2.985

II MICROMETER TUBE WALL THICKNESS MEASUREMENTS (Averaged, in inches)

Panel No.	Original Tubes				Initial Test Panel Tubes										Replacement Panel Tubes			
	No.1 FS	No.1 CS	No.2 FS	No.2 CS	ITP-1 FS	ITP-1 CS	ITP-2 FS	ITP-2 CS	ITP-3 FS	ITP-3 CS	ITP-4 FS	ITP-4 CS	ITP-5 FS	ITP-5 CS	RP-1 FS	RP-1 CS	RP-2 FS	RP-2 CS
3	.308	.306	.301	.306	.294	.295	.305	.307	.293	.293	.288	.319	--	--	.310	.306	.308	.309
4	.306	.310	.317	.314			.289	.307	.280	.295	.312	.312	.297	.299	.301	.321	.311	.305
5	.303	.311	.305	.311	.303	.292	.316	.305	.288	.306	.308	.306	--	--	.313	.310	.300	.315
6	.313	.303	.302	.315	.273	.308	.298	.312	--	--	.310	.307	.289	.306	.310	.309	.301	.317
7	.281	.306	.302	.310	.284	.309	.313	.304	--	--	.293	.310	.302	.310	.302	.315	.306	.312

III TUBE HARDNESS MEASUREMENTS (R_b, Av.)

Panel No.	Original Tubes				Initial Test Panel Tubes										Replacement Panel Tubes			
	No.1 FS	No.1 CS	No.2 FS	No.2 CS	ITP-1 FS	ITP-1 CS	ITP-2 FS	ITP-2 CS	ITP-3 FS	ITP-3 CS	ITP-4 FS	ITP-4 CS	ITP-5 FS	ITP-5 CS	RP-1 FS	RP-1 CS	RP-2 FS	RP-2 CS
3	77.0	77.0	74.0	74.5	75.8	76.0	74.5	74.7	74.5	75.3	76.0	76.2	--	--	79.3	79.3	79.0	78.8
4	75.0	75.0	75.2	75.5			75.8	75.8	72.2	74.8	75.7	74.8	75.8	75.2	78.8	81.0	78.8	80.0
5	75.2	77.3	76.0	76.8	73.3	74.0	74.7	76.5	75.0	75.2	76.7	76.8	--	--	79.7	79.5	81.2	80.7
6	77.5	76.3	76.0	77.3	72.5	73.0	76.0	76.3	--	--	76.8	75.7	75.5	75.2	79.3	81.7	81.7	81.8
7	74.2	74.8	74.8	73.8	75.2	74.3	78.8	75.7	--	--	75.2	75.0	75.5	75.0	79.3	80.2	79.8	78.5

NOTE: Original Tubes Nos. 1, 2 — 5 year exposure

Replacement Panel Nos. 3, 4, 5, 6, 7 - 6 months exposure

Panel Nos. 2,3,5,8
ITP-2, ITP-1 - 17 months exposure
ITP-5, ITP-4, ITP-3 - 23 months exposure

Panel Nos. 1,4,6,7
ITP-5, ITP-4 - 17 months exposure
ITP-3, ITP-2, ITP-1 - 23 months exposure

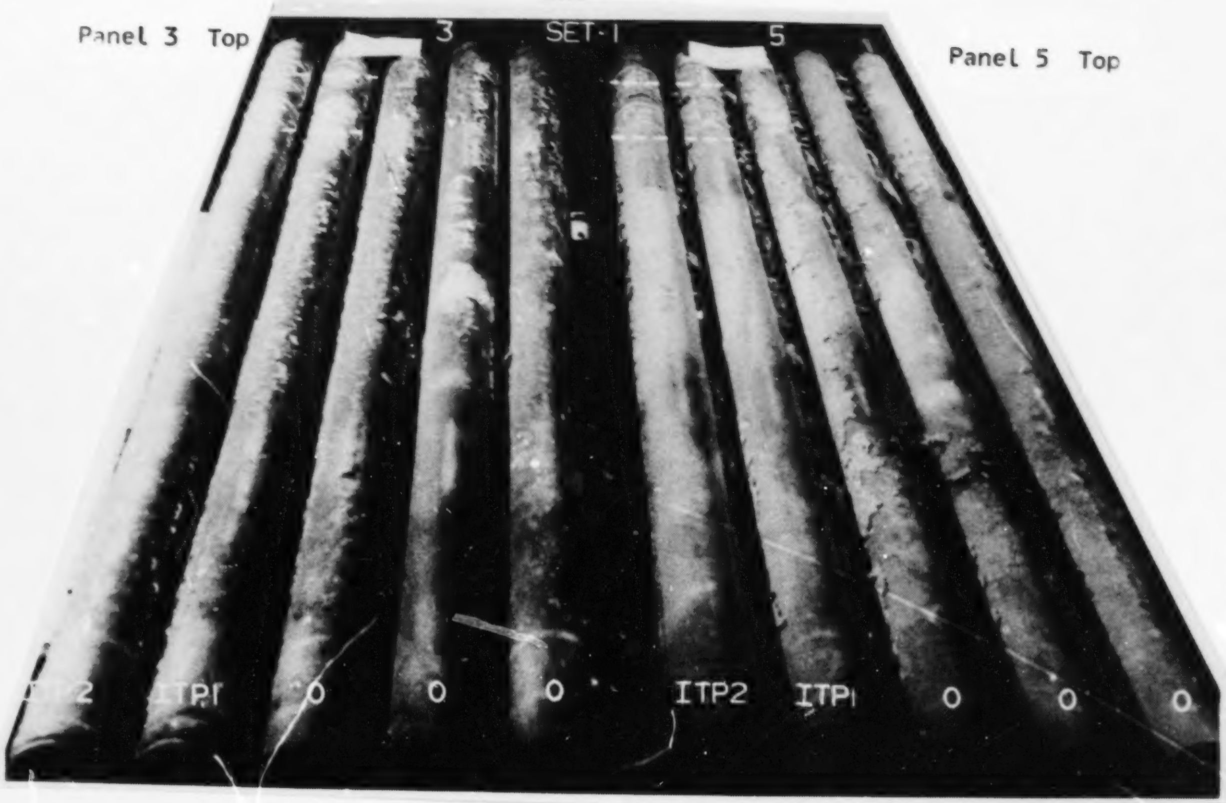

Panel 3 Top
3
SET-1
5
Panel 5 Top
TP2
ITP1
0
0
0
ITP2
ITP1
0
0
0

FIGURE 1

PHOTOGRAPH

AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 3 and 5. Specimens were removed from the two tubes shown at left top of each panel at designated areas. "0" refers to the original furnace tubes while ITP designations denote two of the five tubes in initial test panel installed in May 1976. The two initial test panel tubes were exposed in service for 17 months while the original tubes shown were exposed approximately 5 years.

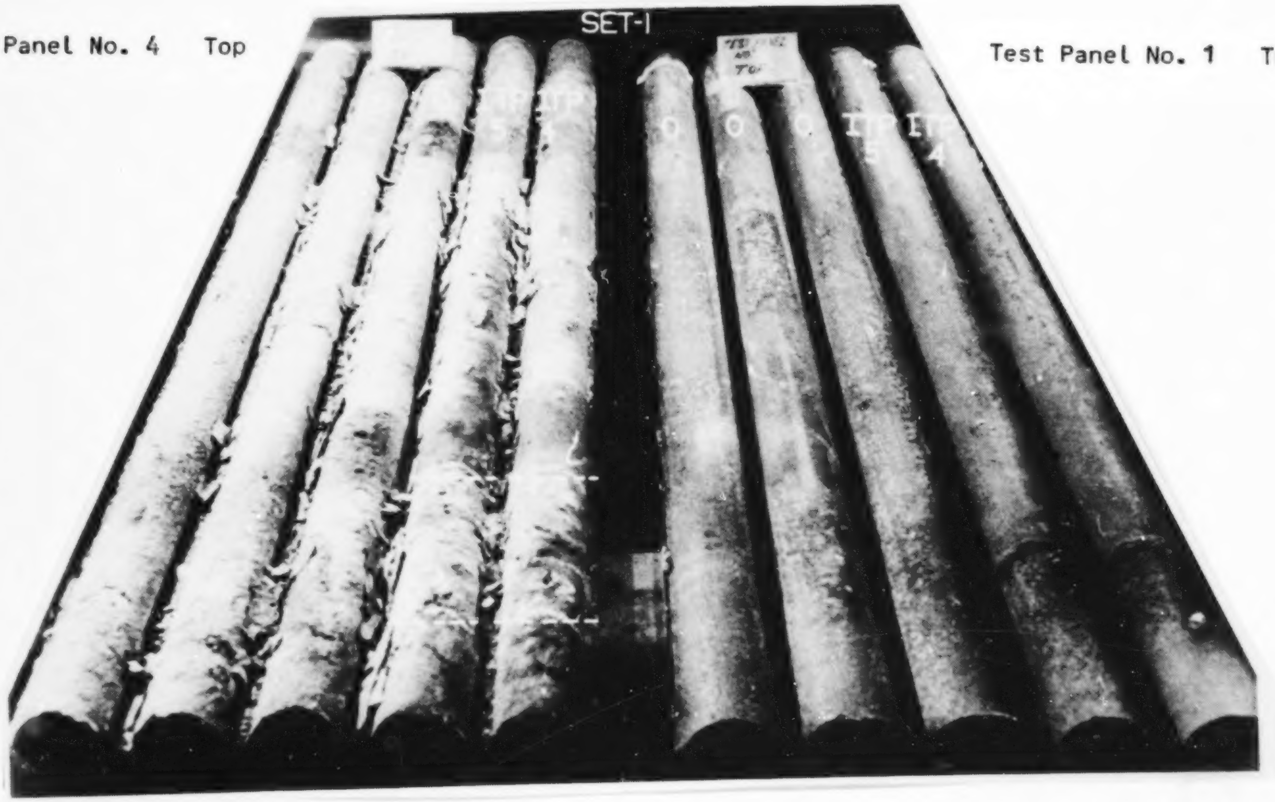

Test Panel No. 4 Top
Test Panel No. 1 Top
SET-1
ITP ITP
5 4
O O O
ITP ITP
5 4

FIGURE 2

PHOTOGRAPH AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 4 and 1. Specimens were removed from the two tubes shown on Panel No. 4 at left at designated areas. No specimens were removed from tubes in Panel No. 1, shown at the right. "O" designations refer to original furnace tubes while ITP denotes two of the 5 tubes in the initial test panel installed in May 1976. The two initial test panel tubes were exposed in service for 17 months while the original tubes were exposed for approximately 5 years.

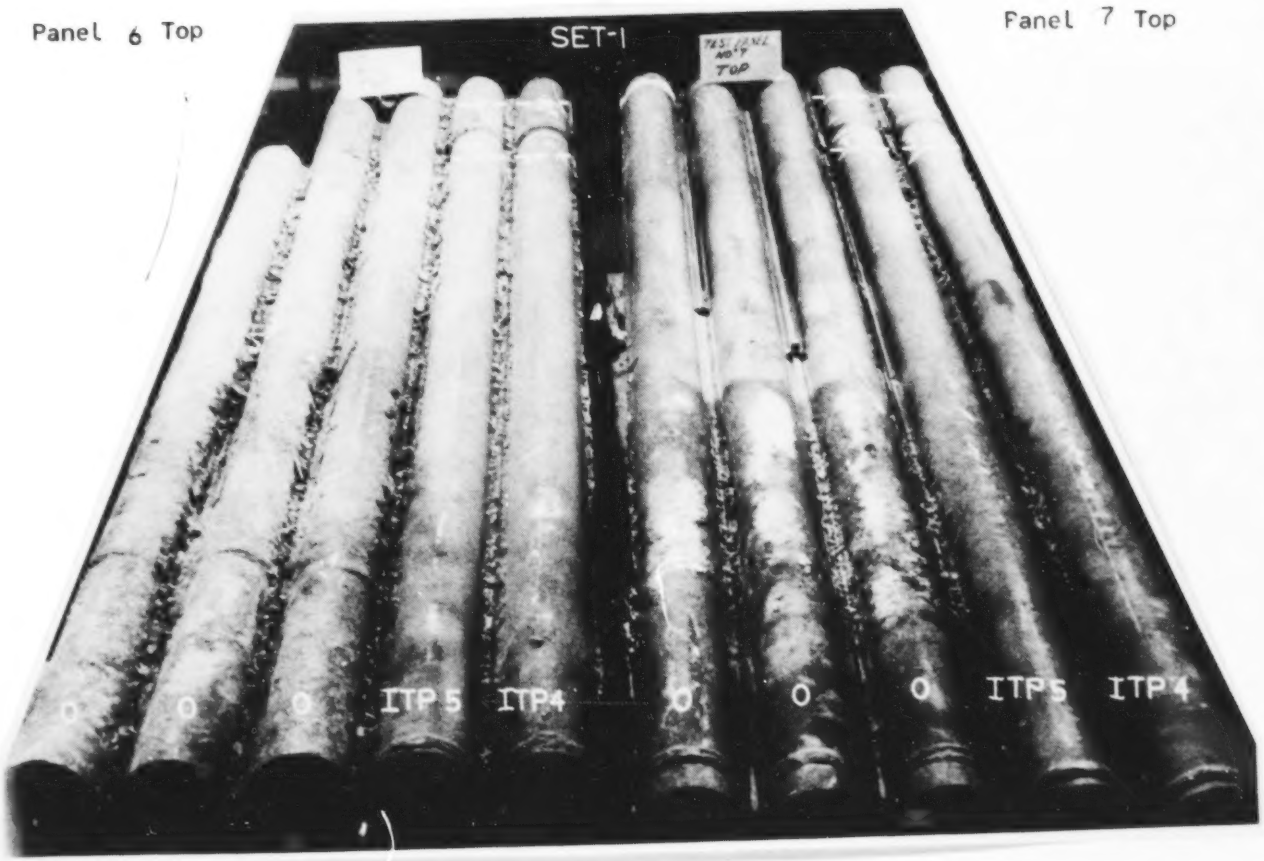

Panel 6 Top
SET-1
TEST PANEL NO 7 TOP
Fanel 7 Top
0
0
0
ITP 5
ITP4
0
0
0
ITP5
ITP 4

FIGURE 3

PHOTOGRAPH

AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 6 and 7 Specimens were removed from two tubes in each panel at designated areas. "O" designations refer to original furnace tubes while ITP denotes two of the five tubes in the initial test panel installed in May 1976. The two initial test pan tubes were exposed in service for 17 months. The original tubes were exposed ap proximately 5 years.

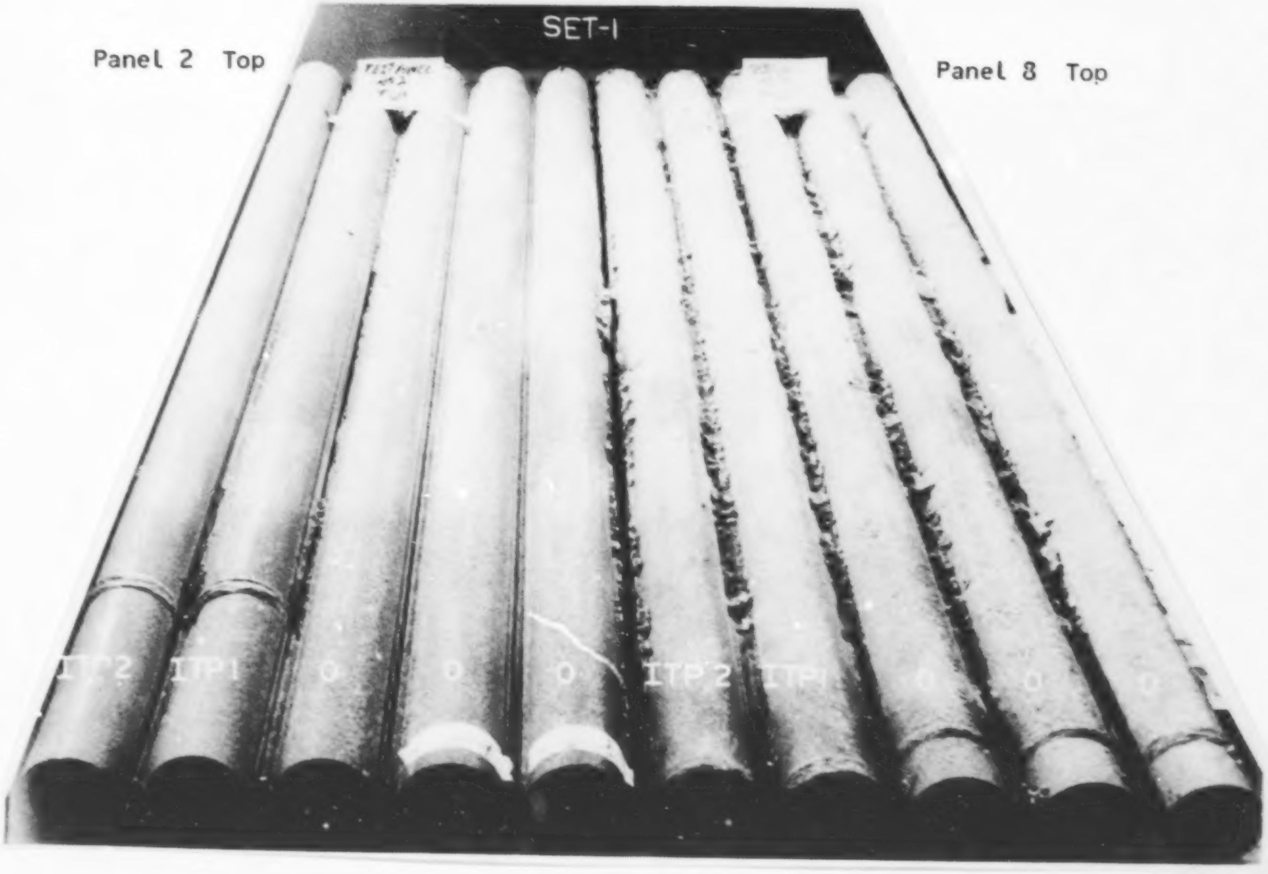

Panel 2 Top
SET-I
Panel 8 Top
TEST PANEL #2 TOP
ITP2
ITP1
0
0
0
ITP2
ITP1
0
0
0

FIGURE 4

PHOTOGRAPH AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 2 and 8. No specimens were removed from these test panels.

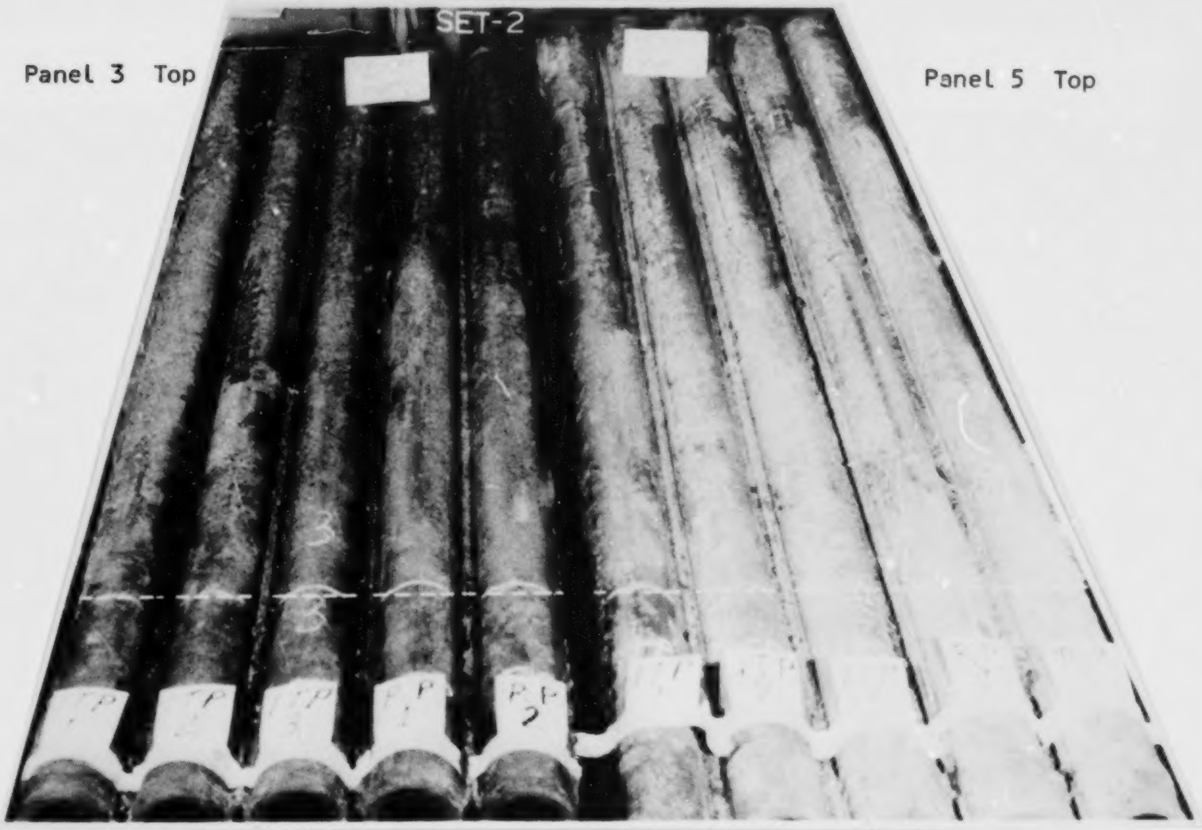


FIGURE 5

PHOTOGRAPH AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 3 and 5 and the locations where specimens were removed for metallurgical examination. The ITP tubes represent the remaining three tubes of the initial test panels installed in May 1976. The RP tubes represent two of the five replacement panel tubes installed in October 1977. The ITP tubes were in service approximately 23 months and the replacement tubes 6 months.

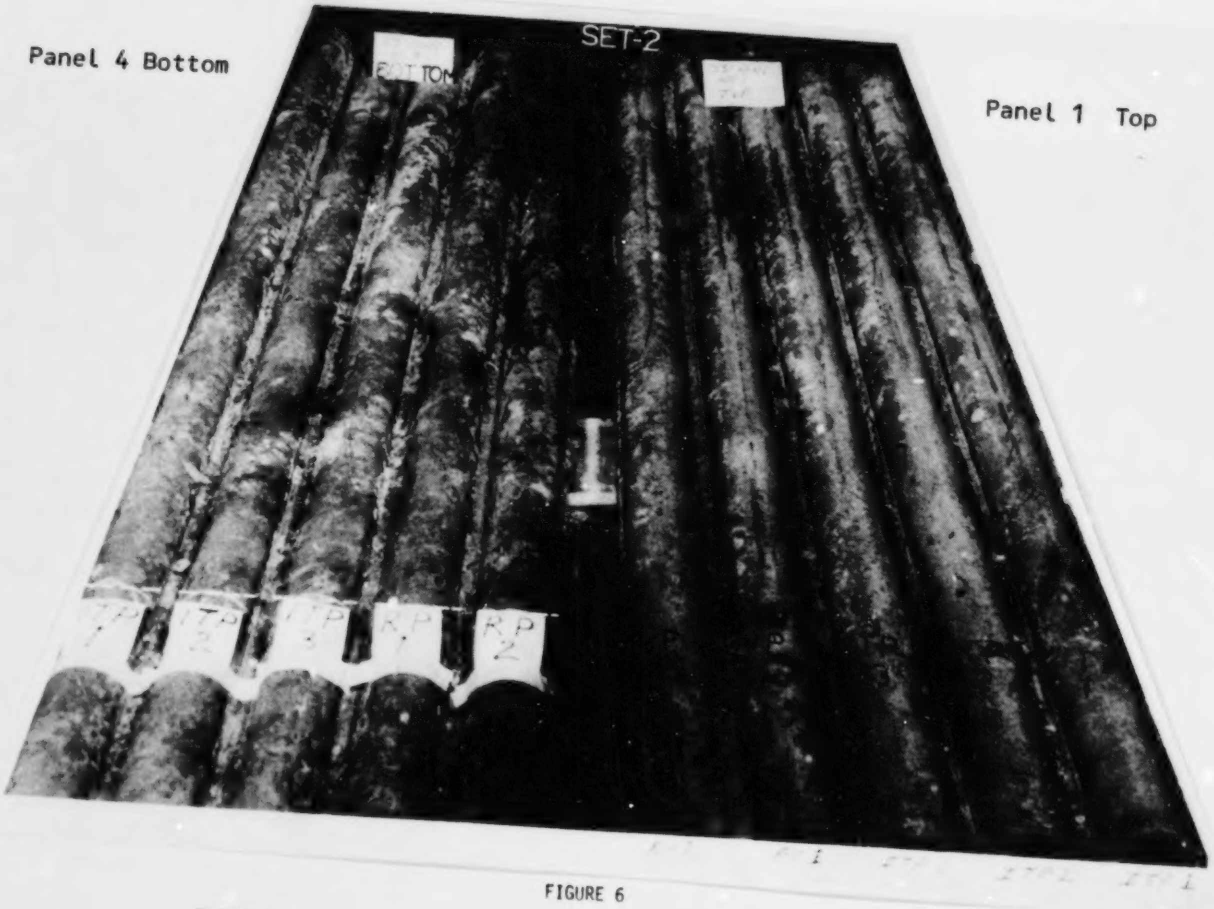

Panel 4 Bottom
Panel 1 Top
SET-2
BOTTOM
ITP 1
ITP 2
ITP 3
RP 1
RP 2

FIGURE 6

PHOTOGRAPH

AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 4 and 1. Specimens were removed only from tubes in Panel No. 4 at indicated locations. The ITP tubes represent the remaining three tubes in the initial test panels installed in May 1976. The RP tubes represent two of the five replacement panel tubes installed in October 1977. The ITP tubes were in service approximately 23 months and the replacement tubes 6 months.

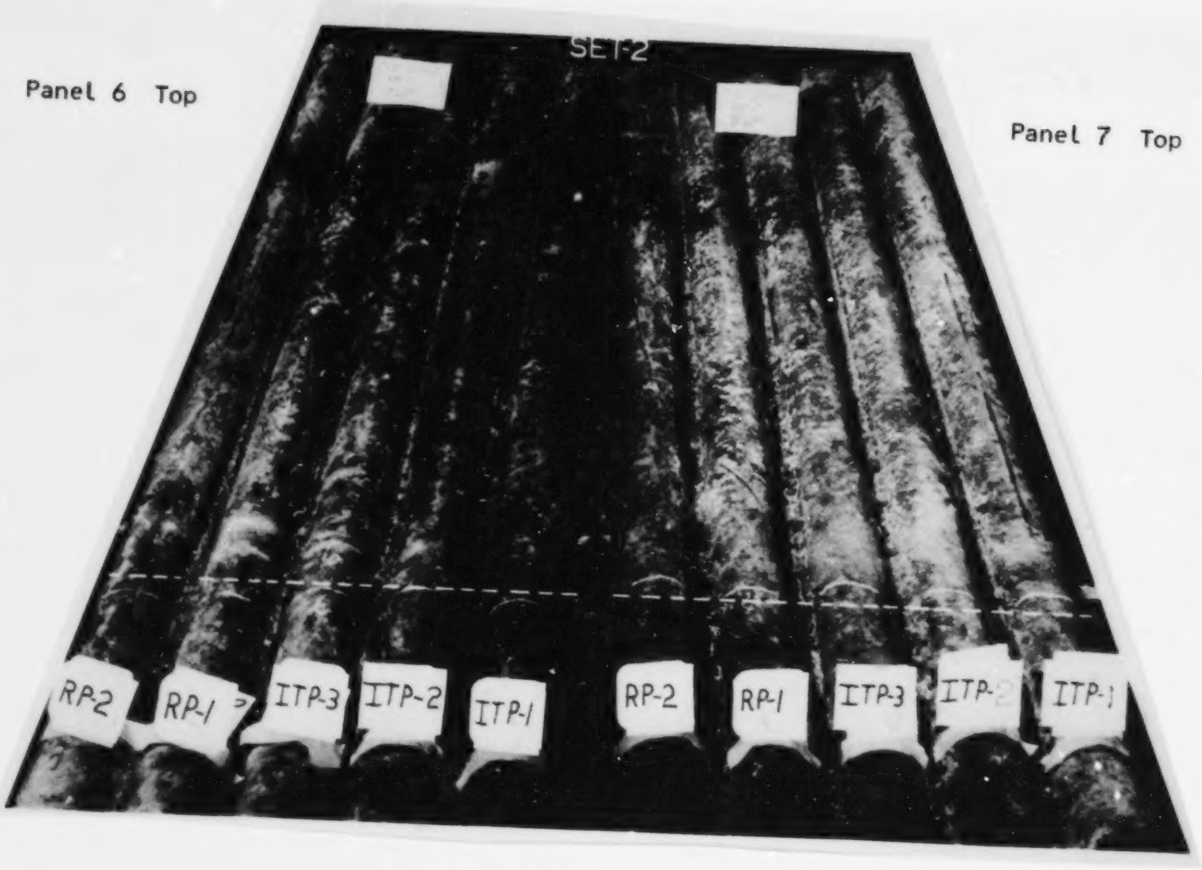

Panel 6 Top
SET-2
Panel 7 Top
RP-2
RP-1
ITP-3
ITP-2
ITP-1
RP-2
RP-1
ITP-3
ITP-2
ITP-1

FIGURE 7

PHOTOGRAPH

AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 6 and 7. and the locations where specimens were removed. The ITP tubes represent the remaining three tubes in the initial test panels installed in May 1976. The RP tubes represent two of the five tubes in the replacement panel installed in October 1977. The ITP tubes were in service approximately 23 months and the replacement tubes 6 months.

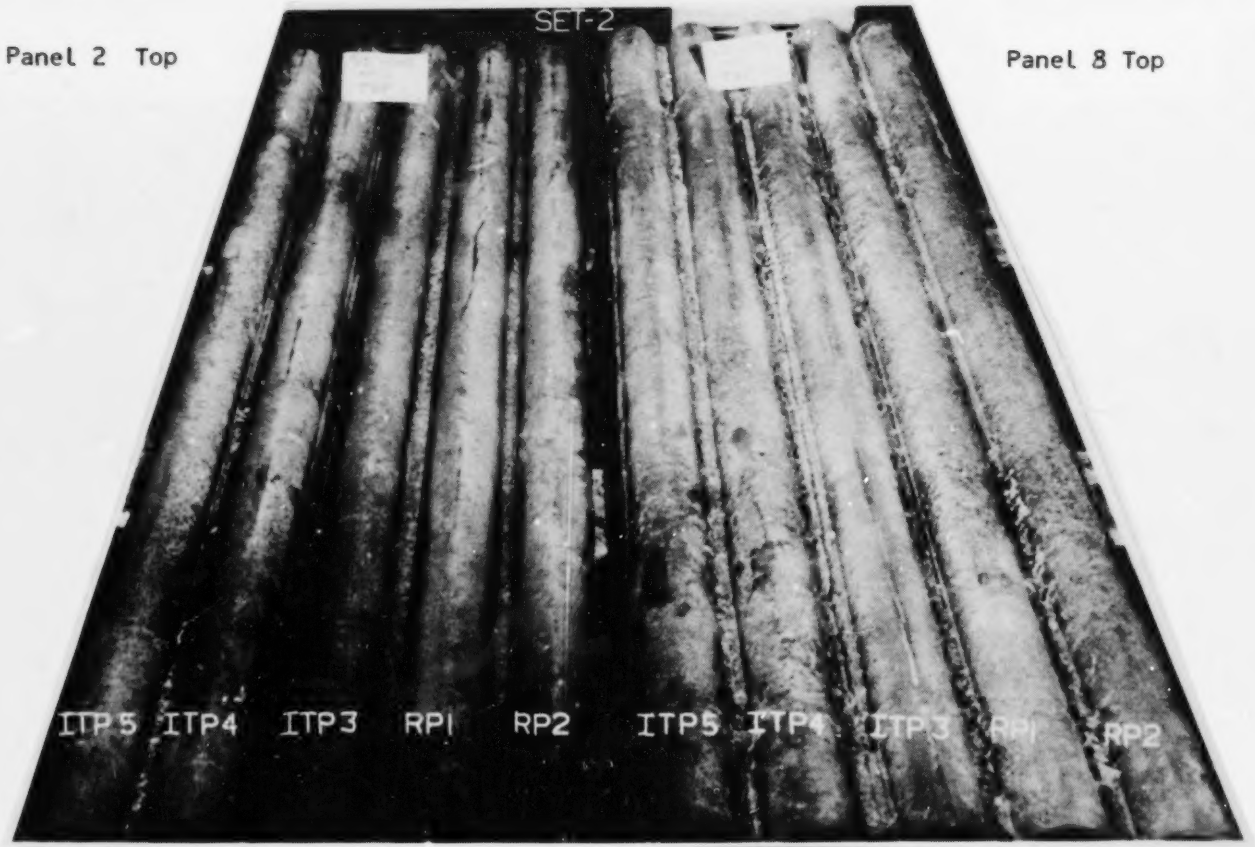

Panel 2 Top
Panel 8 Top
SET-2
ITP5
ITP4
ITP3
RP1
RP2
ITP5
ITP4
ITP3
RP1
RP2

FIGURE 8

PHOTOGRAPH AS RECEIVED

Photograph illustrates the as-received appearances of test Panel Nos. 2 and 8. The ITP tubes represent the remaining three tubes in the initial test panels installed in May 1976. The RP tubes represent two of the five replacement panel tubes installed in October 1977. The ITP tubes were in service for approximately 23 months and the replacement tubes 6 months.

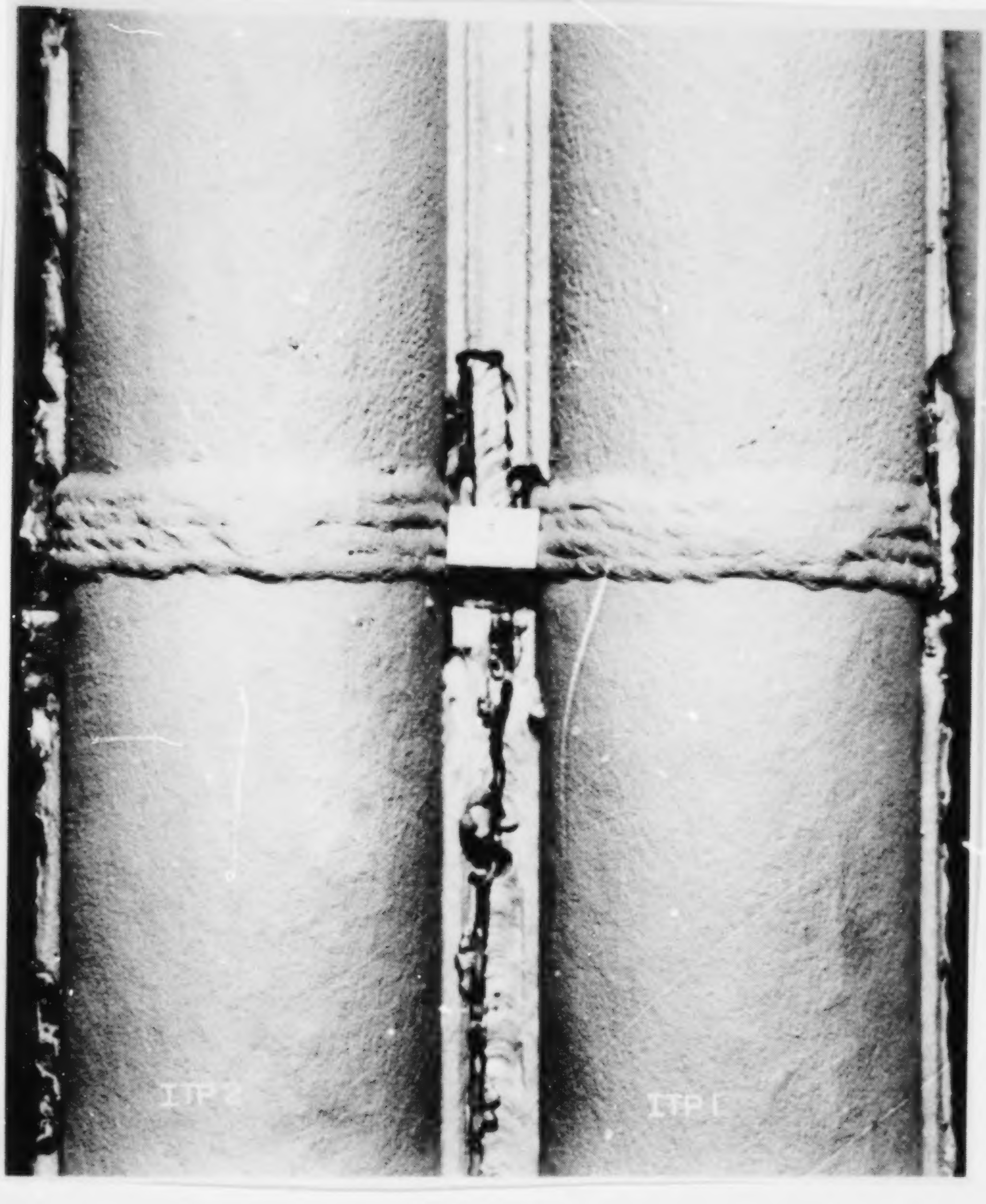


FIGURE 9

PHOTOGRAPH

AFTER ALUMINUM GRIT BLASTING HOT FACES

Photograph illustrates the appearances of underlying hot side tube faces after corrosion products/scale were removed from tubes located in Panel No. 3 (Set 1) at locations shown in Figure 1. Tube sections above the welds are from original furnace tubes while tube sections below the welds are from the initial test panels installed in May 1976.

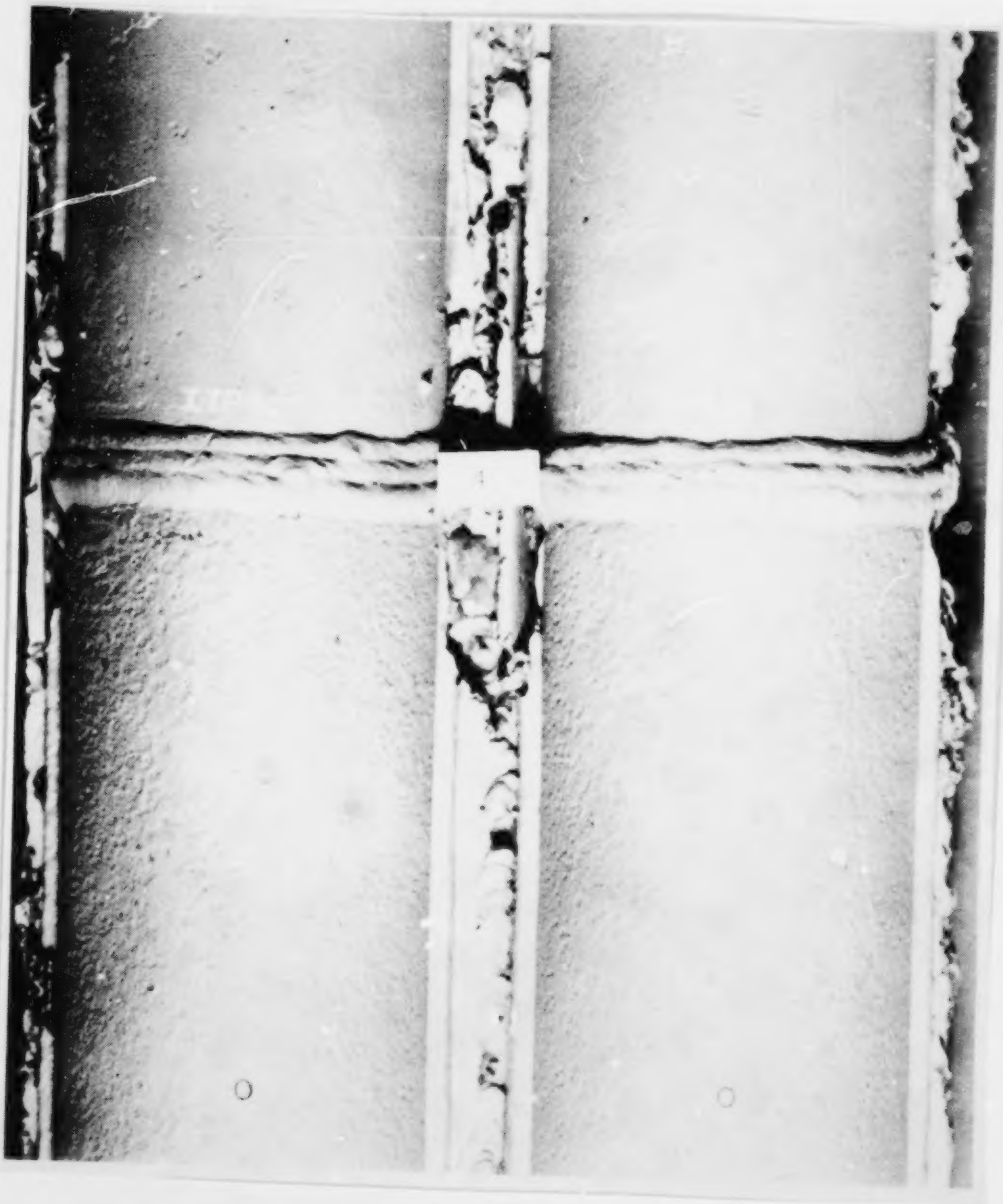


FIGURE 10

PHOTOGRAPH

AFTER ALUMINUM GRIT BLASTING HOT FACES

Photograph illustrates the appearances of underlying hot side tube faces after corrosion products/scale were removed from tubes located in Panel No. 4 (Set 1) at locations shown in Figure 2. Tube sections above the welds are from the initial test panels installed in May 1976 while the sections below the welds are from original furnace tubes.

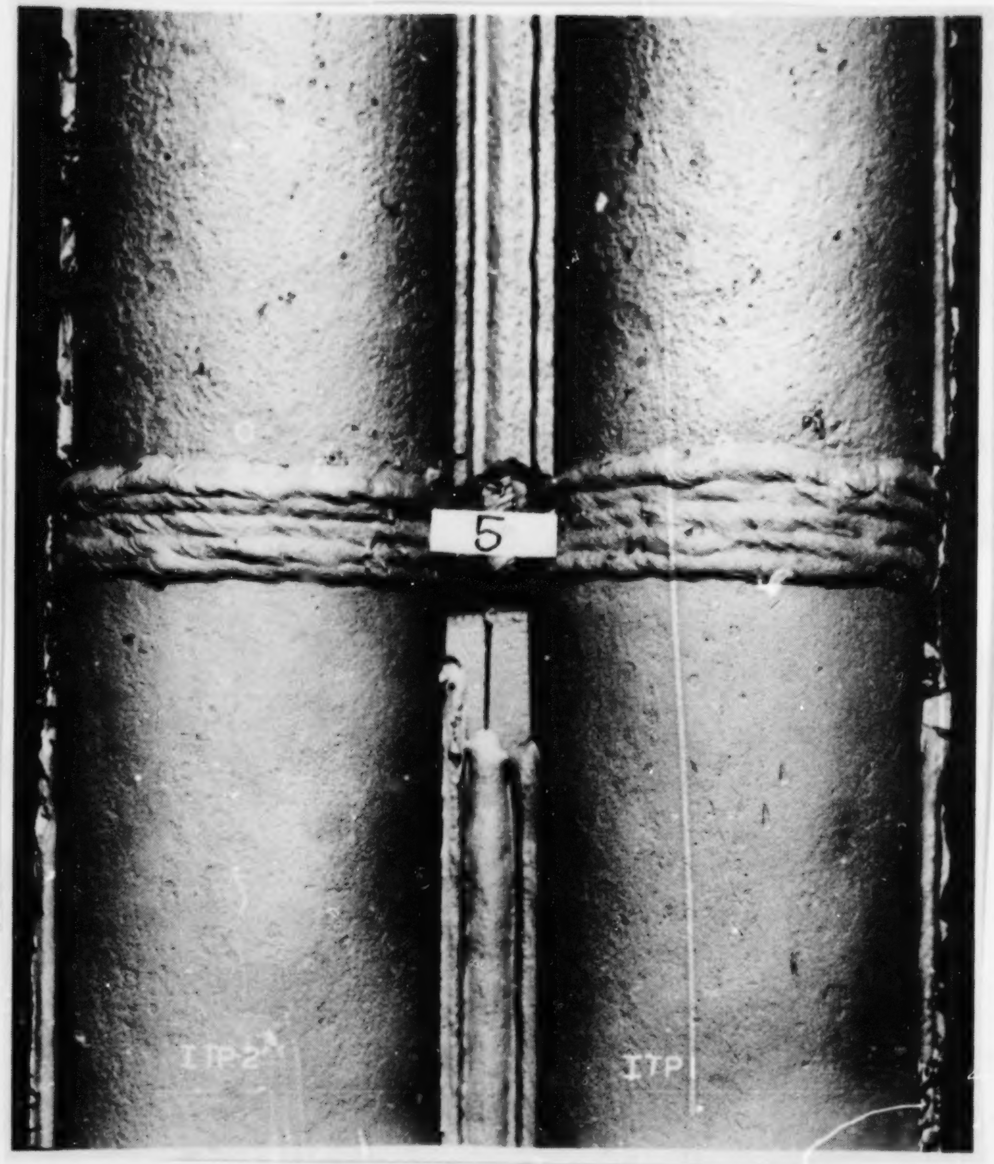


FIGURE 11

PHOTOGRAPH AFTER ALUMINUM GRIT BLASTING HOT FACES

Photograph illustrates the appearances of underlying hot side tube faces after corrosion products/scale were removed from tubes located in Panel No. 5 (Set 1) at locations shown in Figure 1. Tube sections above the welds are from the original furnace tubes while the tube sections shown below the welds are from the initial test panels installed in May 1976. The original tubes were in service approximately 5 years, while the initial test panel tubes were in service approximately 17 months.

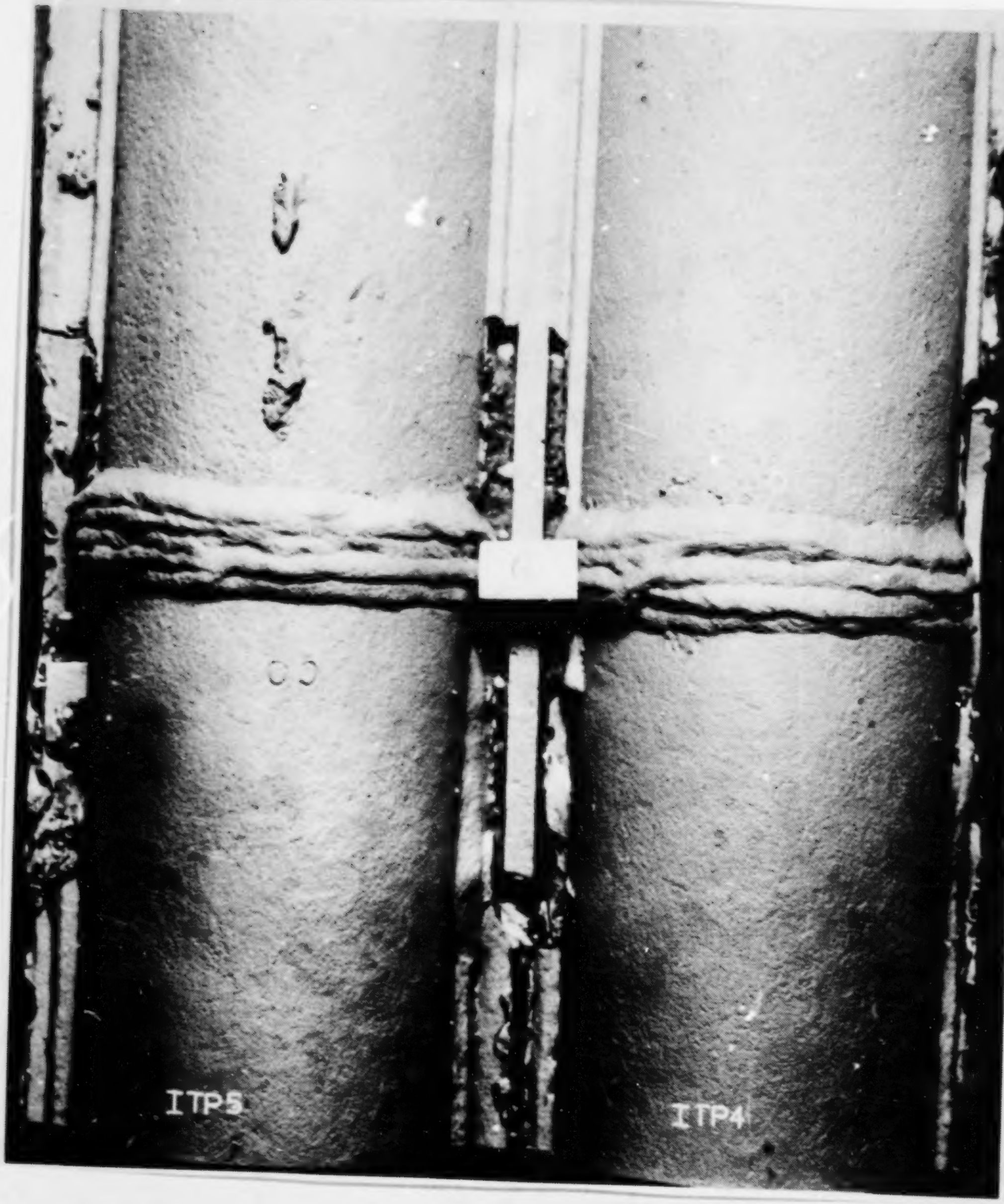


FIGURE 12

PHOTOGRAPH AFTER ALUMINUM GRIT BLASTING HOT FACES

Photograph illustrates the appearances of underlying hot side tube faces after corrosion products/scale were removed from the tubes located in Panel No. 6 (Set 1) at locations shown in Figure 3. Tube sections above the welds are from original furnace tubes while tube sections below the welds are from the initial test panels installed in May 1976.

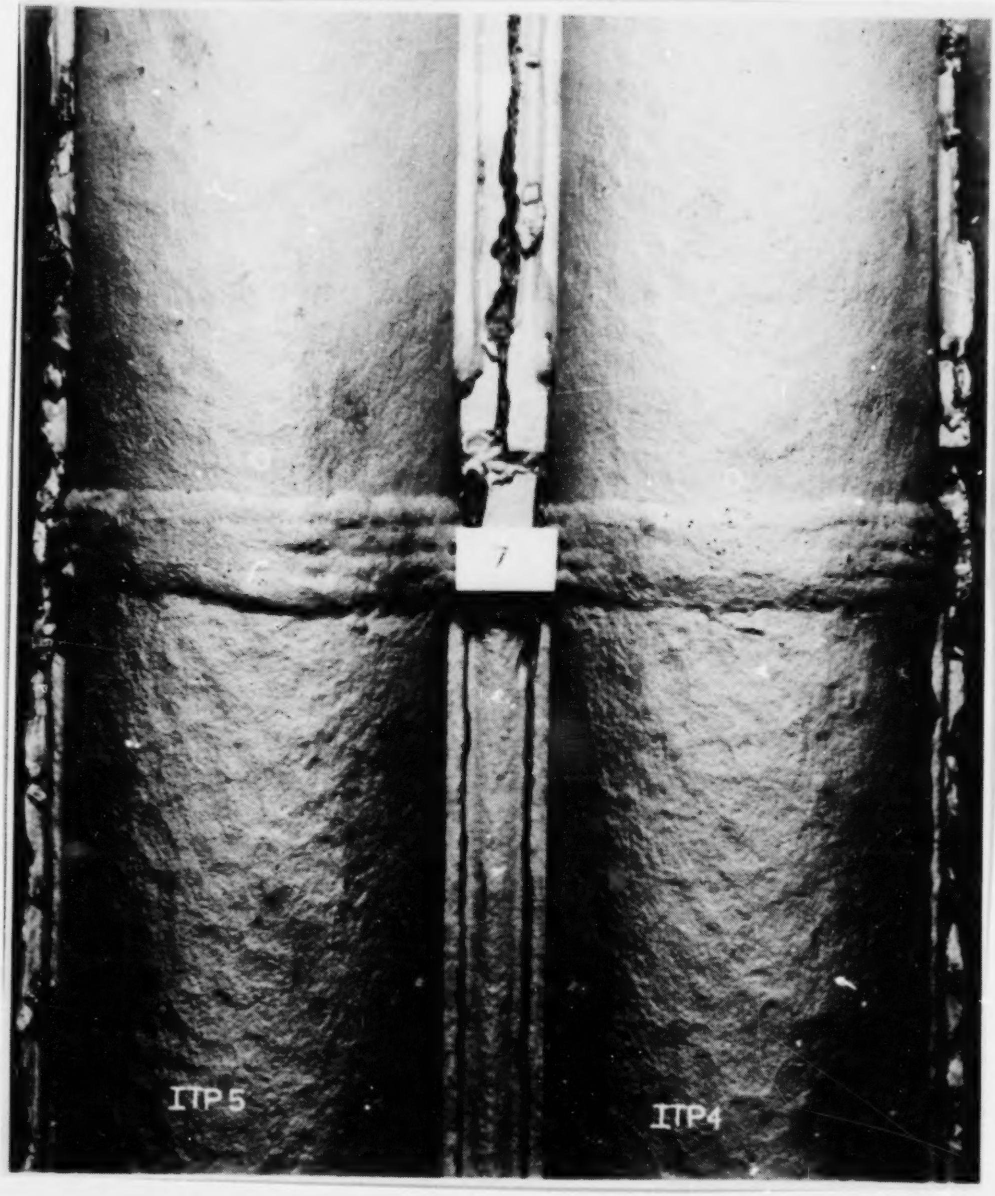


FIGURE 13

PHOTOGRAPH AFTER ALUMINUM GRIT BLASTING HOT FACES

Photograph illustrates the appearances of underlying hot side tube faces after corrosion products/scale were removed from tubes located in Panel No. 7 (Set 1) at locations shown in Figure 3. Tube sections above the welds are from original furnace tubes while tube sections below the welds are from the initial test panels installed in May 1976.

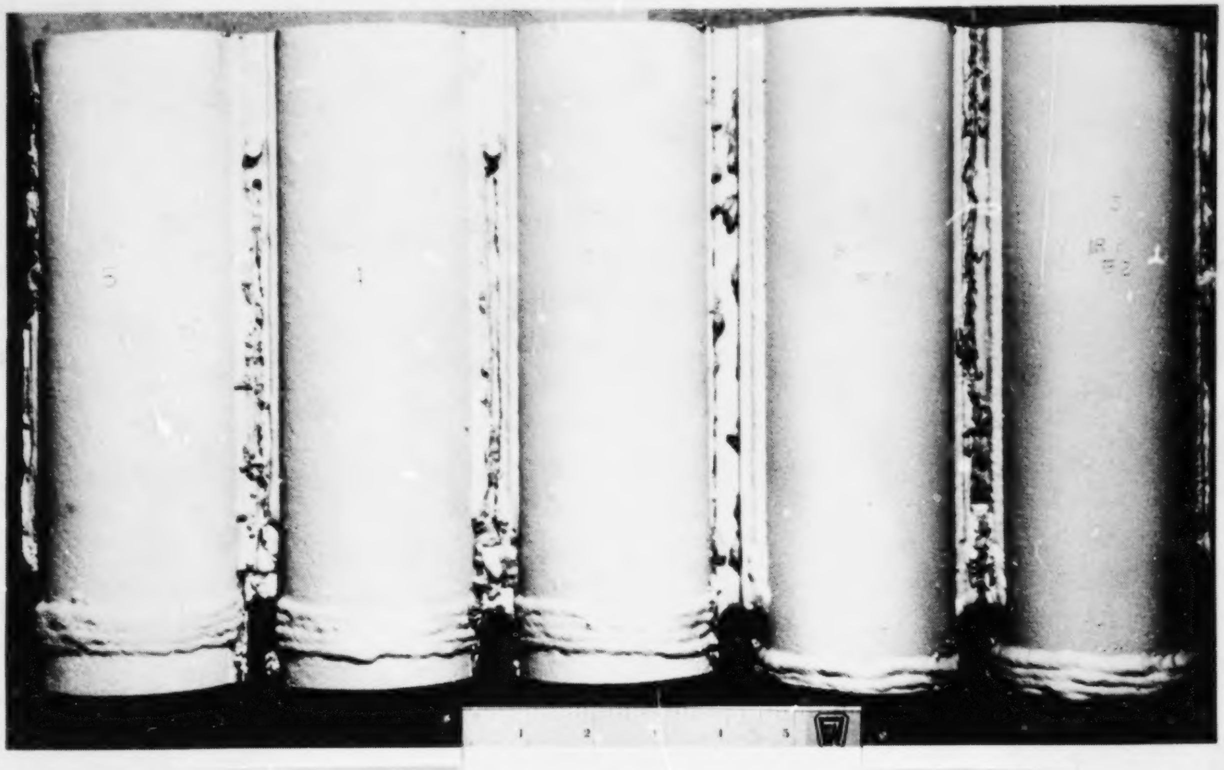


FIGURE 14

PHOTOGRAPH AFTER ALUMINUM GRIT BLASTING HOT FACES

Photograph illustrates the appearances of underlying fire side tube faces after corrosion products/scale were removed from tubes in Panel No. 3 (Set 2). The ITP specimens were exposed for 23 months service and the RP specimens were exposed for approximately 6 months.

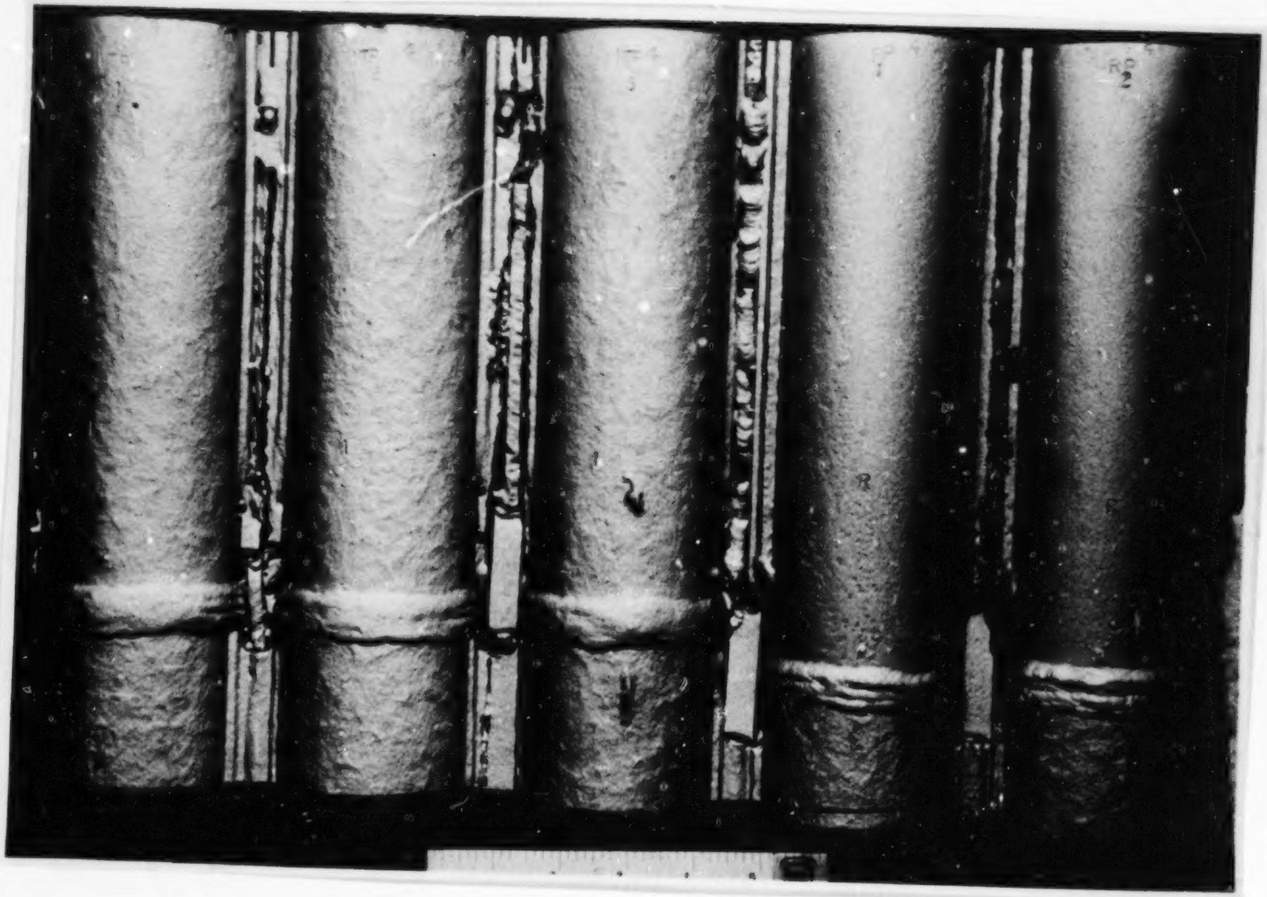


FIGURE 15

PHOTOGRAPH

AFTER ALUMINUM GRIT BLASTING HOT FACES

Photograph illustrates the appearances of underlying fireside tube faces after corrosion products/scale were removed from tubes in Panel No. 4 (Set 2). The ITP specimens were exposed for 23 months service and the RP specimens were exposed for approximately 6 months.

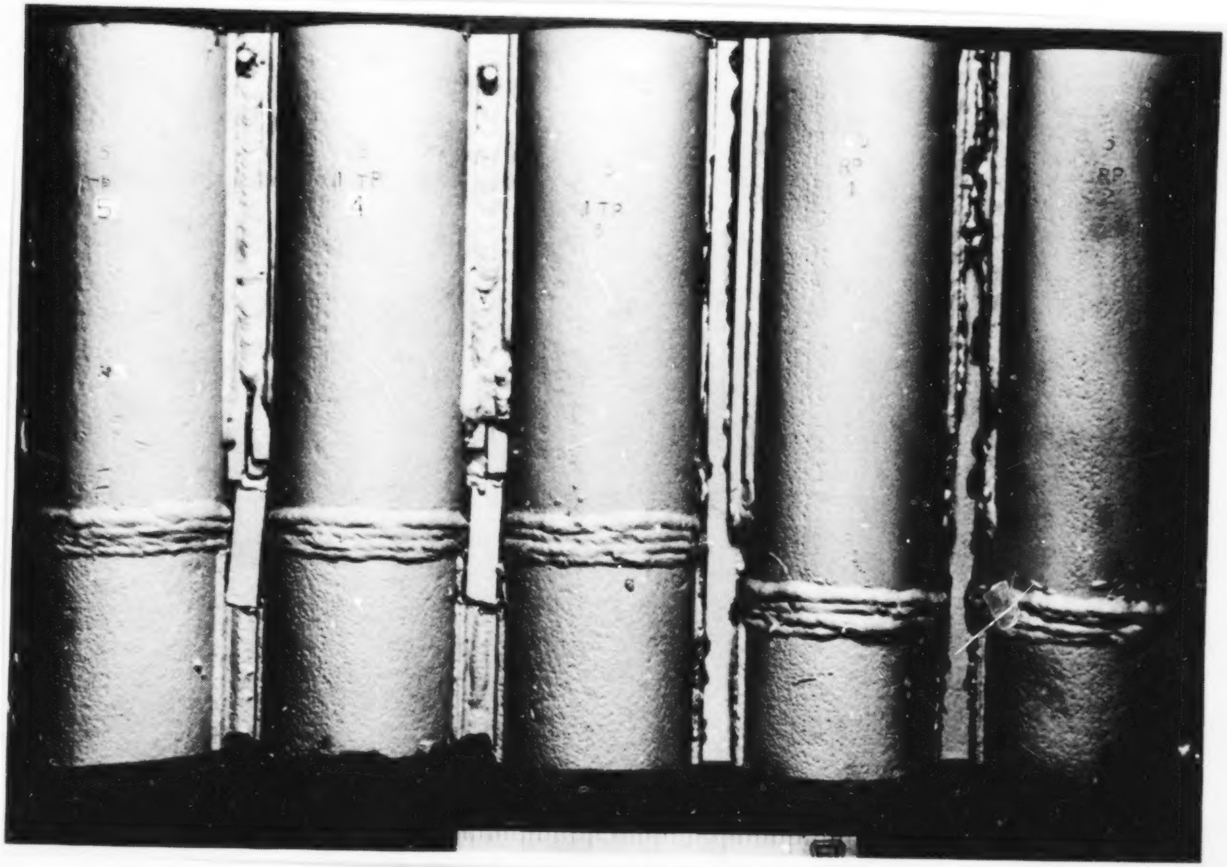


FIGURE 16

PHOTOGRAPH

AFTER ALUMINUM GRIT BLASTING FIRESIDE FACES

Photograph illustrates the appearances of underlying fireside tube faces after corrosion products/scale were removed from tubes in Panel No. 5 (Set 2). The ITP specimens were exposed for 23 months service and the RP specimens were exposed for approximately 6 months.

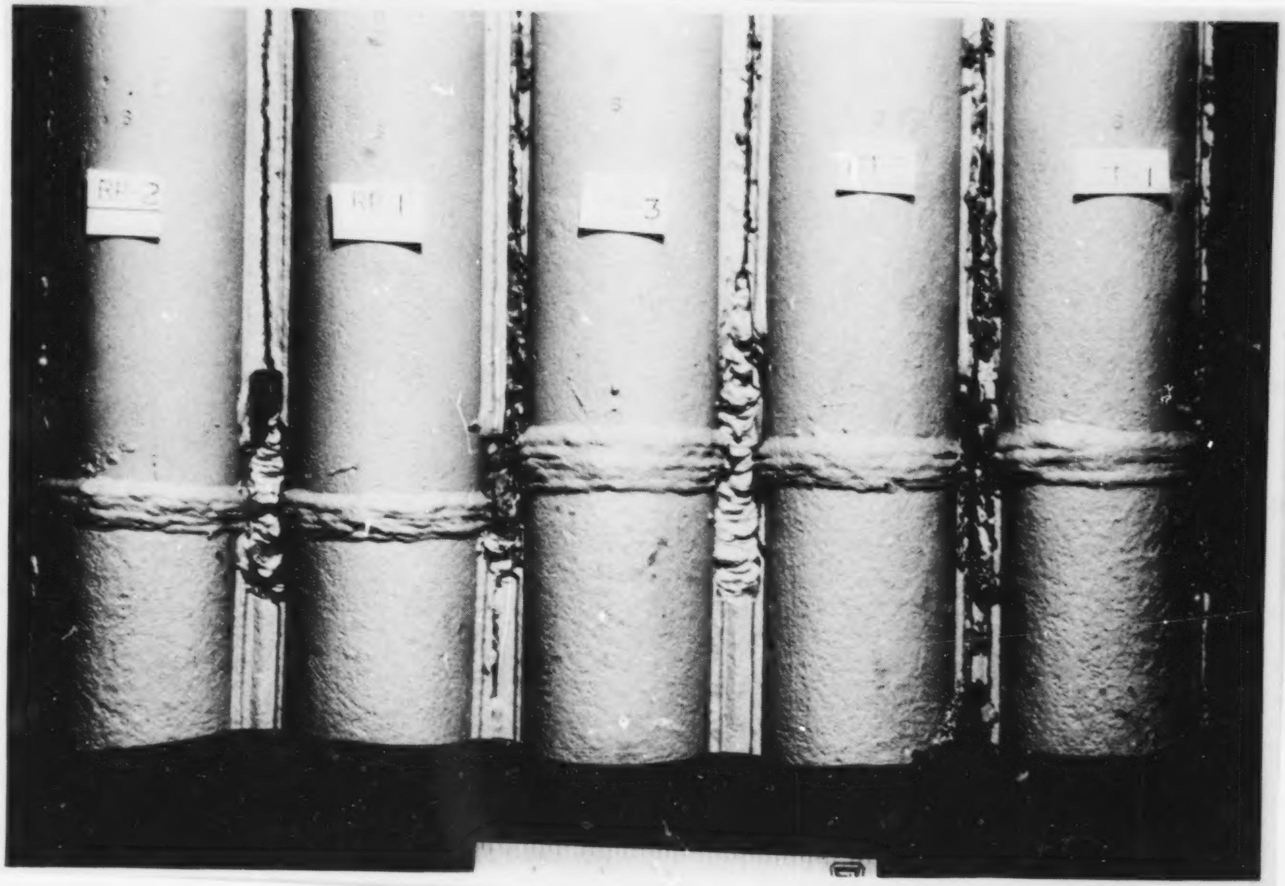


FIGURE 17

PHOTOGRAPH AFTER ALUMINUM GRIT BLASTING FIRESIDE FACES

Photograph illustrates the appearances of underlying fireside tube faces after corrosion products/scale were removed from tubes located in Panel No. 6 (Set 2). The ITP specimens were exposed for 23 months and the RP specimens were exposed for approximately 6 months.

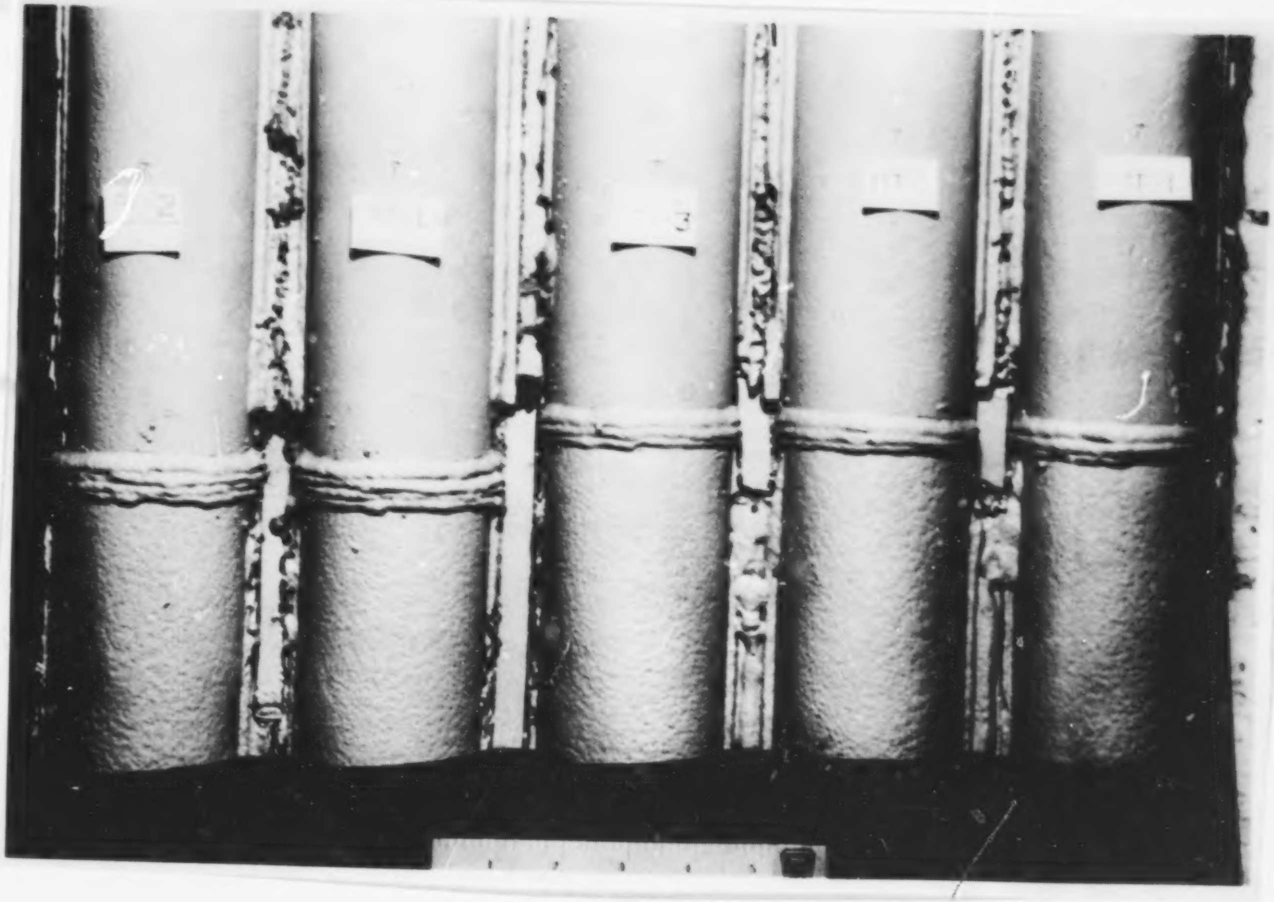


FIGURE 18

PHOTOGRAPH

AFTER ALUMINUM GRIT BLASTING FIRESIDE FACES

Photograph illustrates the appearances of underlying fireside tube faces after corrosion products/scale were removed from tubes located in Panel No. 7 (Set 2). The ITP specimens were exposed for 23 months service and the RP specimens were exposed for approximately 6 months.

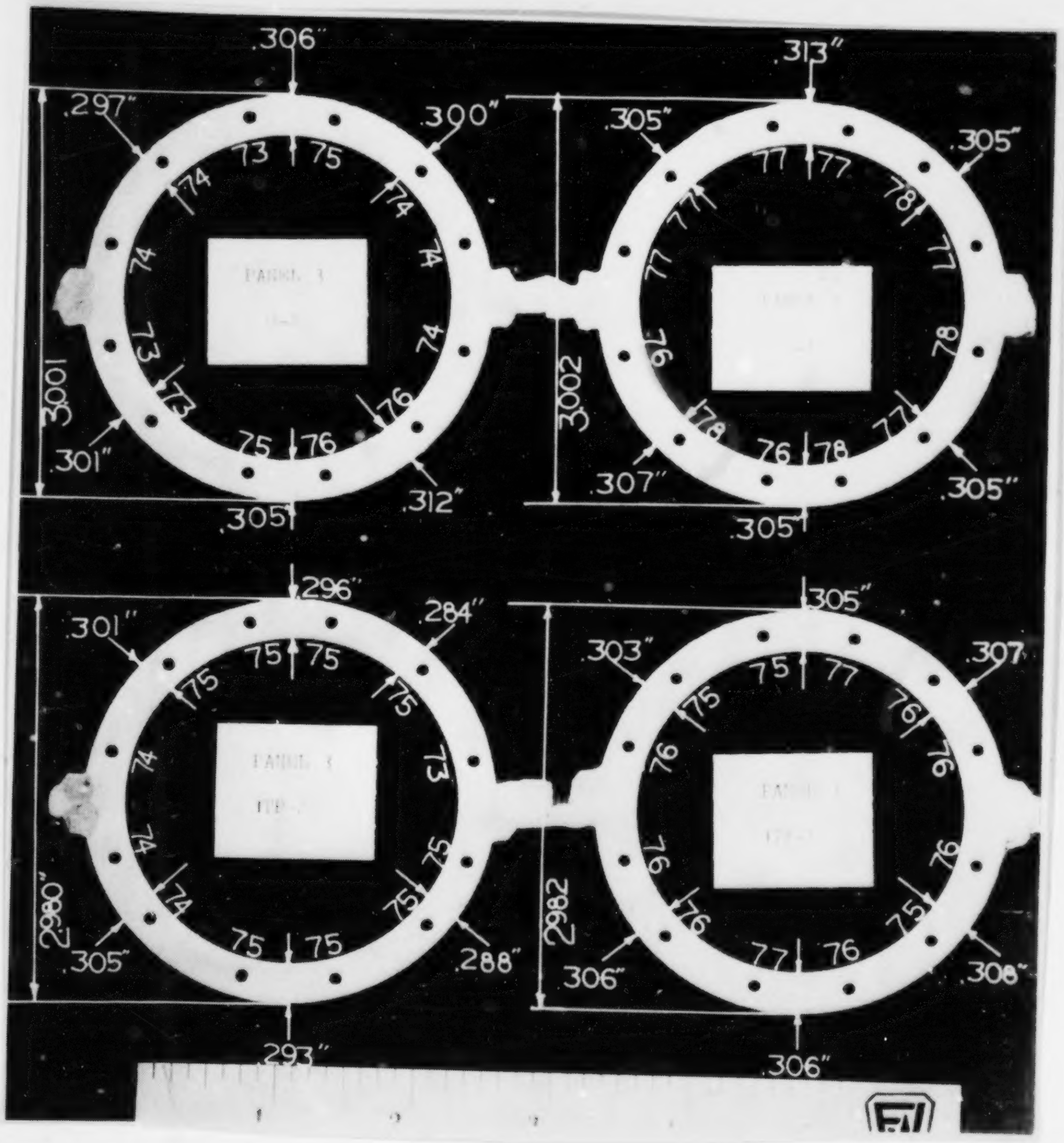

.306"
.297"
.300"
73
75
74
74
74
74
74
73
73
73
76
75
76
3.001
.301"
.305
.312"
PANEL 3
.313"
.305"
.305"
77
77
77
78
77
77
76
78
78
77
76
78
3.002
.307"
.305"
.305
.296"
.301"
.284"
75
75
75
75
74
73
74
75
74
75
75
75
2.980"
.305"
.288"
.293"
PANEL 3
.305"
.303"
.307
75
77
75
76
76
76
76
76
76
75
77
76
2.982
306"
.308"
.306"

FIGURE 19

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of original furnace tubes

BOTTOM: Transverse sections of initial test panel tubes

Photomacrograph illustrates the appearances of transverse ring sections removed from Panel No. 3 (Set 1) shown in Figure 9.

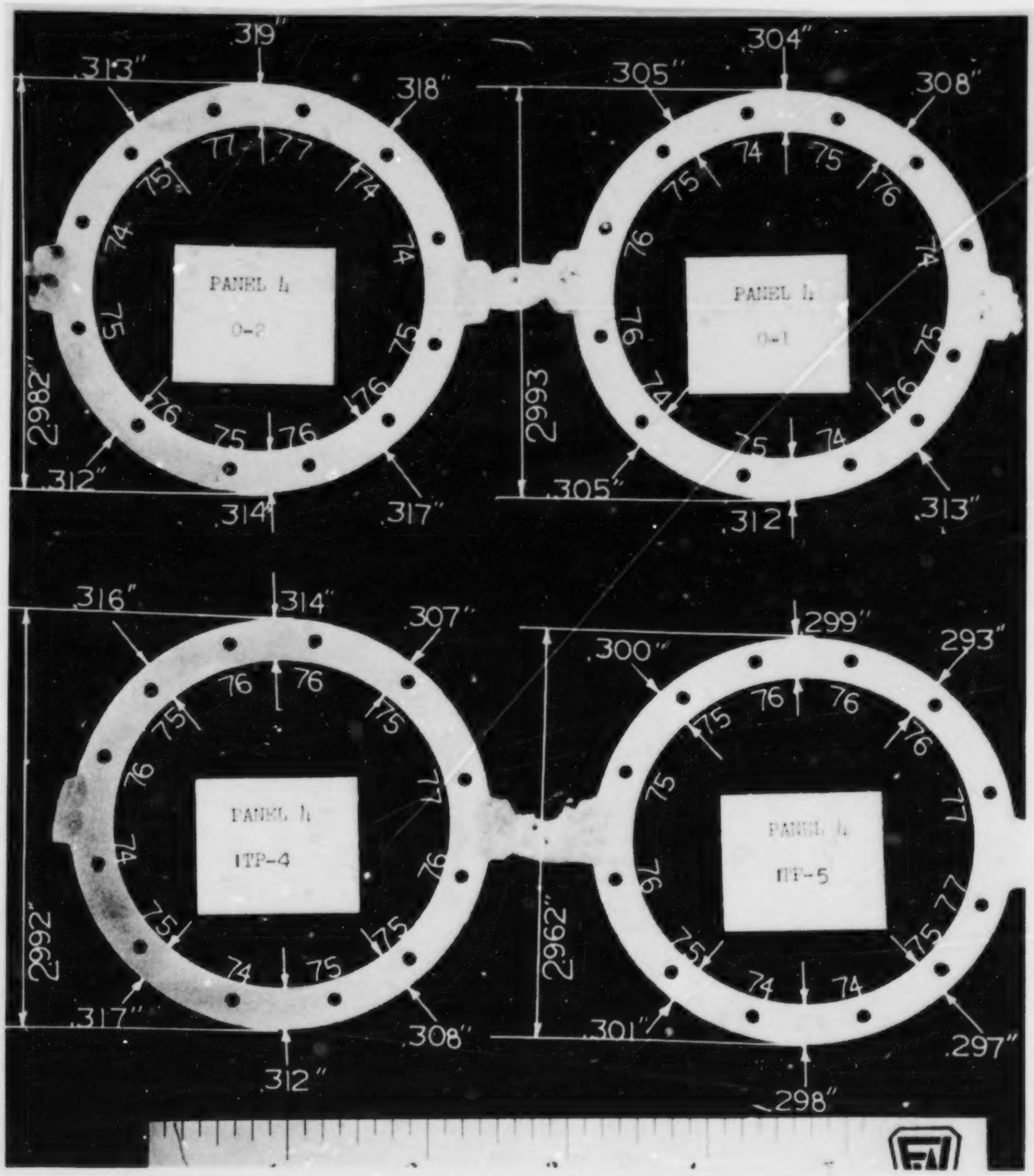

.319"
.313"
.318"
77
77
75
74
74
74
75
75
76
76
75
76
PANEL 4
O-2
2982"
.312"
.314"
.317"
.304"
.305"
.308"
74
75
75
76
76
74
76
75
74
76
75
74
PANEL 4
O-1
2993
.305"
.312
.313"
.316"
.314"
.307"
76
76
75
75
76
77
74
76
75
75
74
75
PANEL 4
ITP-4
2992"
.317"
.308"
.312"
.299"
.300"
.293"
75
76
76
76
75
77
76
77
75
75
74
74
PANEL 4
ITP-5
2962"
.301"
.297"
.298"

FIGURE 20

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of original furnace tubes
BOTTOM: Transverse sections of initial test panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from Panel No. 4 (Set 1) shown in Figure 10.

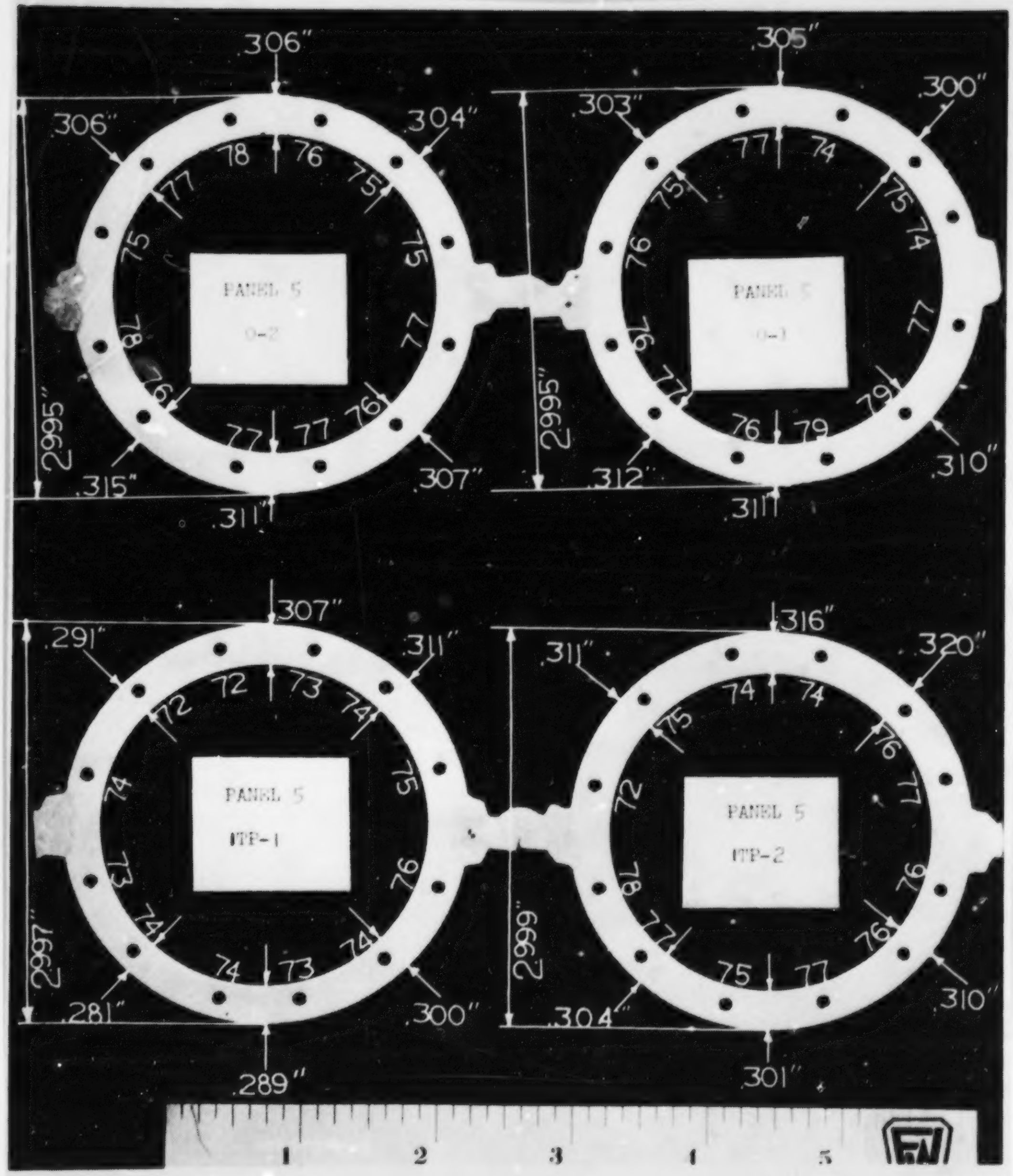

.306"
.305"
.306"
.304"
.303"
.300"
78
76
77
74
77
75
75
75
74
75
75
76
PANEL 5
O-2
PANEL 5
O-1
78
77
76
77
76
77
77
76
77
79
79
76
2995"
2995"
.315"
.307"
.312"
.310"
.311"
.311"
.307"
.316"
.291"
.311"
.311"
.320"
72
72
73
74
74
74
75
76
74
75
72
77
PANEL 5
ITP-1
PANEL 5
ITP-2
73
76
78
76
74
74
77
76
74
73
75
77
2997"
2999"
.281"
.300"
.304"
.310"
.289"
.301"
1
2
3
4
5

FIGURE 21

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of original furnace tubes
BOTTOM: Transverse sections of initial test panel tubes

Photomacrograph illustrates the appearances of transverse ring sections removed from Panel No. 5 (Set 1) shown in Figure 11.

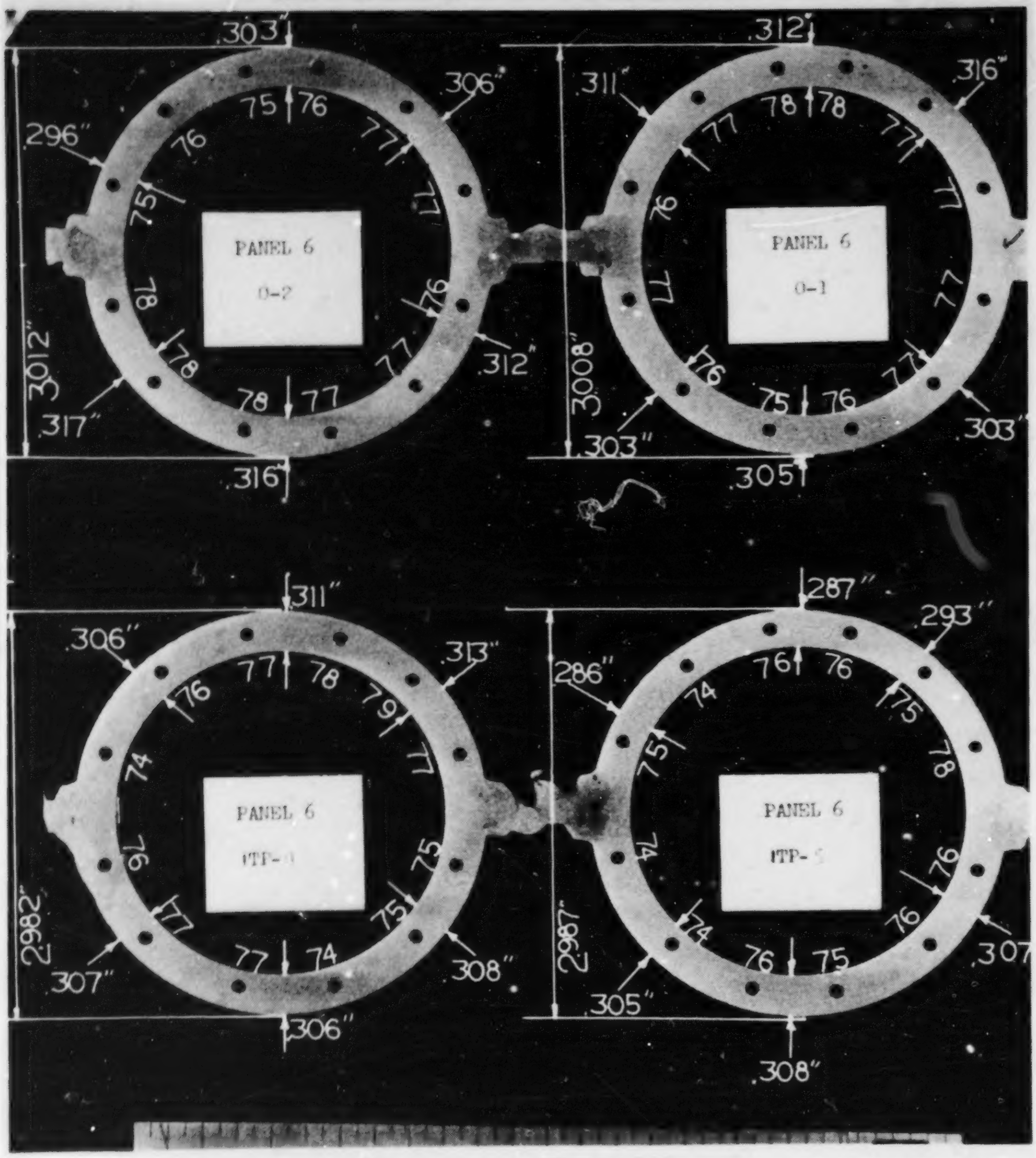

.303"
.306"
.296"
75 76
76
77
77
75
PANEL 6
O-2
78
76
3.012"
78
.312"
.317"
78 77
77
.316"
.312"
.311"
.316"
78 78
77
77
77
76
PANEL 6
O-1
77
77
3.008"
76
77
.303"
75 76
.303"
.305"
.311"
.306"
.313"
77 78
76
79
74
77
PANEL 6
ITP-
76
75
2.982"
77
75
.307"
77 74
.308"
.306"
.287"
.293"
.286"
76 76
74
75
75
78
PANEL 6
ITP-
74
76
2.987"
74
76
.307
.305"
76 75
.308"

FIGURE 22

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of original furnace tubes.
BOTTOM: Transverse sections of initial test panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from Panel No. 6 (Set 1) shown in Figure 12.

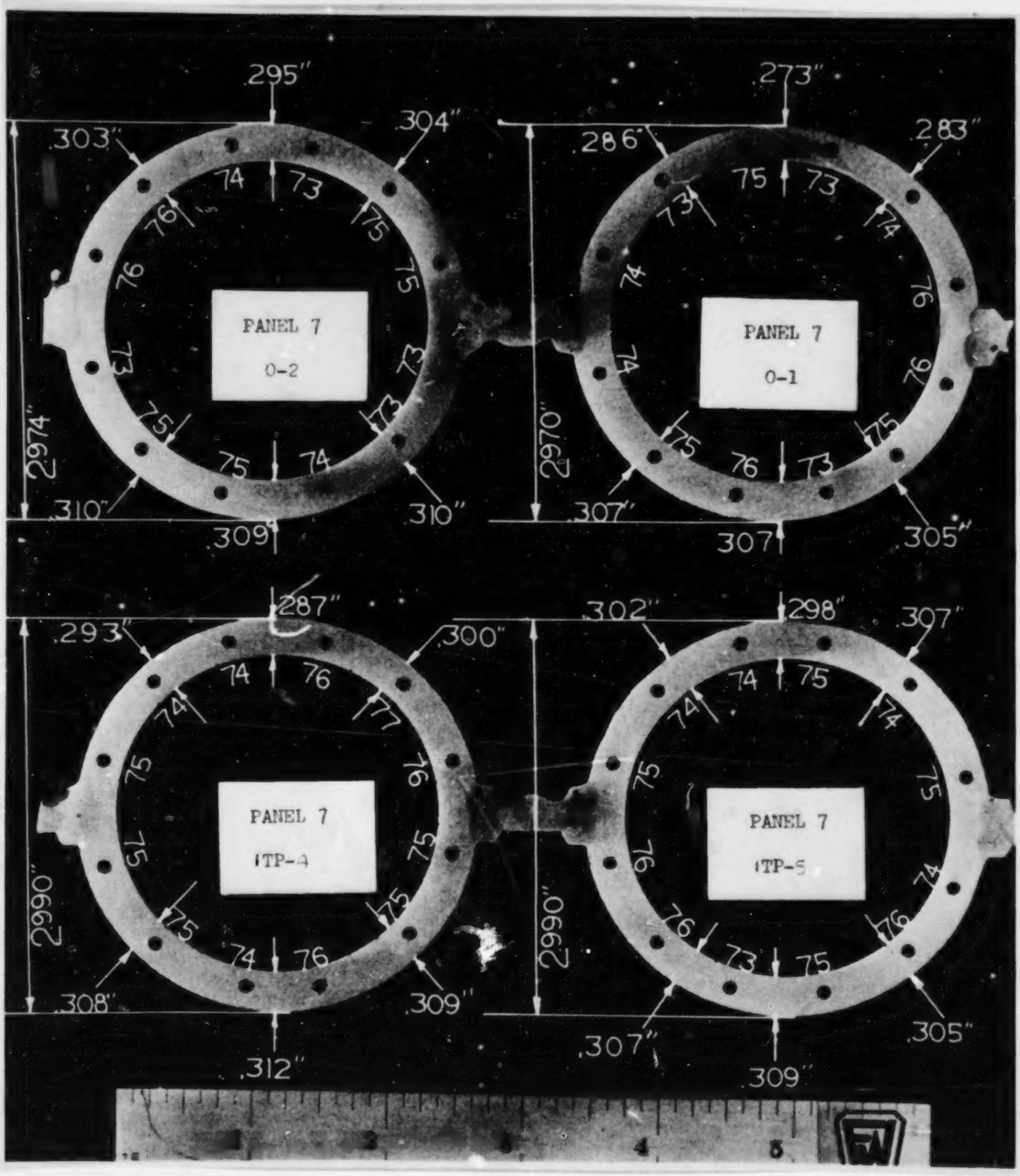

.295"
.303"
.304"
74
73
76
75
76
75
73
73
73
75
75
74
PANEL 7
0-2
2.974"
.310"
.309"
.310"
.273"
.286"
.283"
75
73
73
74
74
76
74
76
75
76
73
75
PANEL 7
0-1
2.970"
.307"
307
.305"
.287"
.293"
.300"
74
76
74
77
75
76
75
75
75
75
74
76
PANEL 7
TP-4
2.990"
.308"
.312"
.309"
.302"
.298"
.307"
74
75
74
74
75
75
76
74
76
76
73
75
PANEL 7
TP-6
2.990"
.307"
.309"
.305"
1
2
3
4
5

FIGURE 23

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of original from original furnace tubes.
BOTTOM: Transverse sections of initial test panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from Panel No. 7 (Set 1) shown in Figure 13.

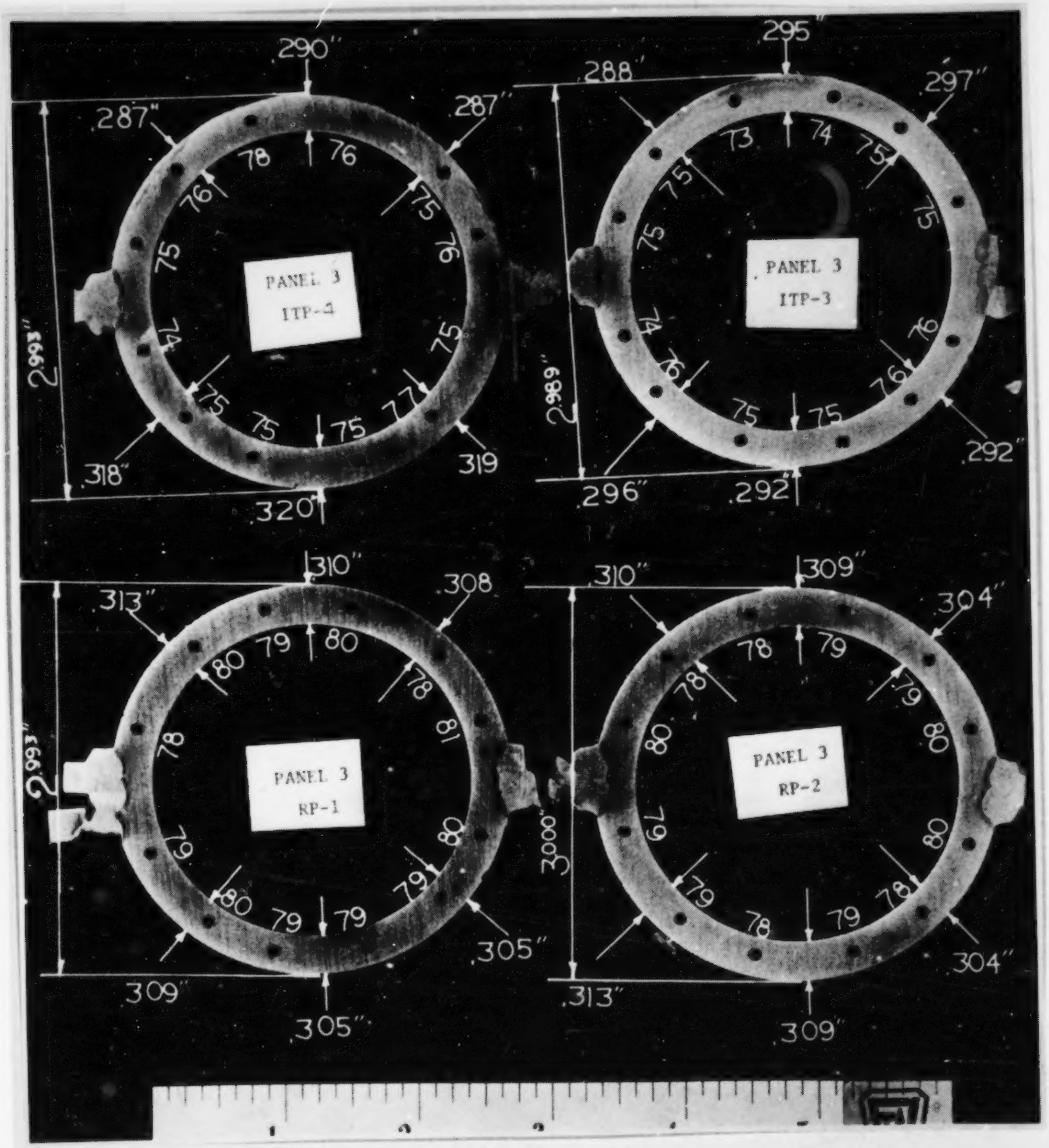
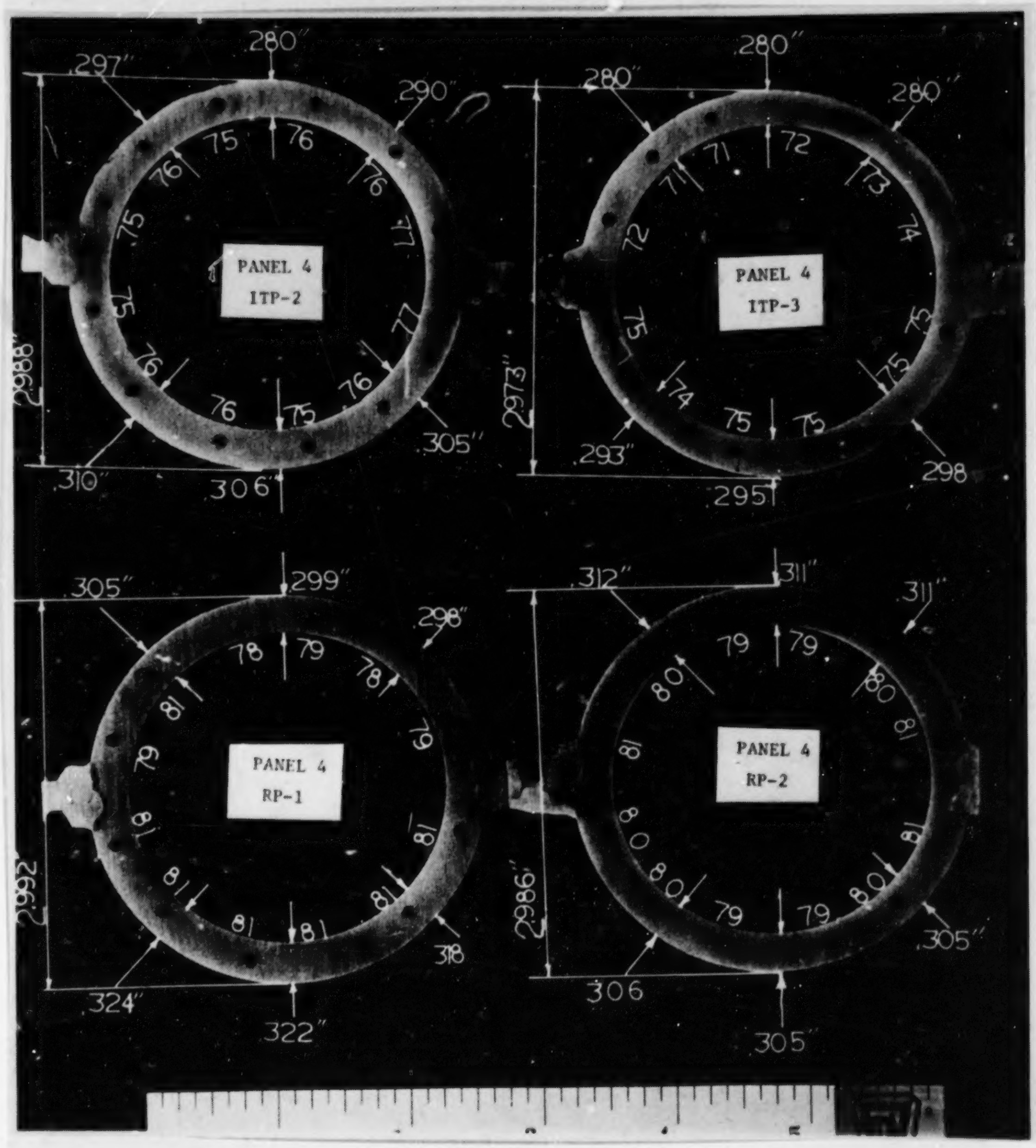

.290"
.287"
.287"
78
76
76
75
76
75
75
74
75
75
75
77
2.993"
.318"
319
.320
PANEL 3
ITP-4
.295"
.288"
.297"
73
74
75
75
75
75
76
74
76
76
75
75
2.989"
.296"
.292"
.292"
PANEL 3
ITP-3
.310"
.313"
.308
80
79
80
78
78
81
79
80
79
79
79
80
2.993"
.309"
.305"
.305"
PANEL 3
RP-1
.310"
.309"
.304"
78
79
78
79
80
80
79
79
78
79
78
80
3.000"
.313"
.309"
.304"
PANEL 3
RP-2

FIGURE 24

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of initial test panel tubes.
BOTTOM: Transverse sections of replacement panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from tubes in Panel No. 3 (Set 2) shown in Figure 14.



.280"
.297"
.290"
75
76
76
76
75
77
75
77
76
76
76
75
PANEL 4
ITP-2
2.988"
.310"
.306"
.305"
.280"
.280"
.280"
71
71
72
73
72
74
75
75
74
75
75
75
PANEL 4
ITP-3
2.973"
.293"
.295
298
.305"
.299"
.298"
78
79
78
81
79
79
81
81
81
81
81
81
PANEL 4
RP-1
2.992"
.324"
.322"
318
.312"
.311"
.311"
79
79
80
80
81
81
80
81
80
80
79
79
80
PANEL 4
RP-2
2.986"
306
.305
.305"

FIGURE 25

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of initial test panel tubes
BOTTOM: Transverse sections of replacement panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from tubes in Panel No. 4 (Set 2) shown in Figure 15.

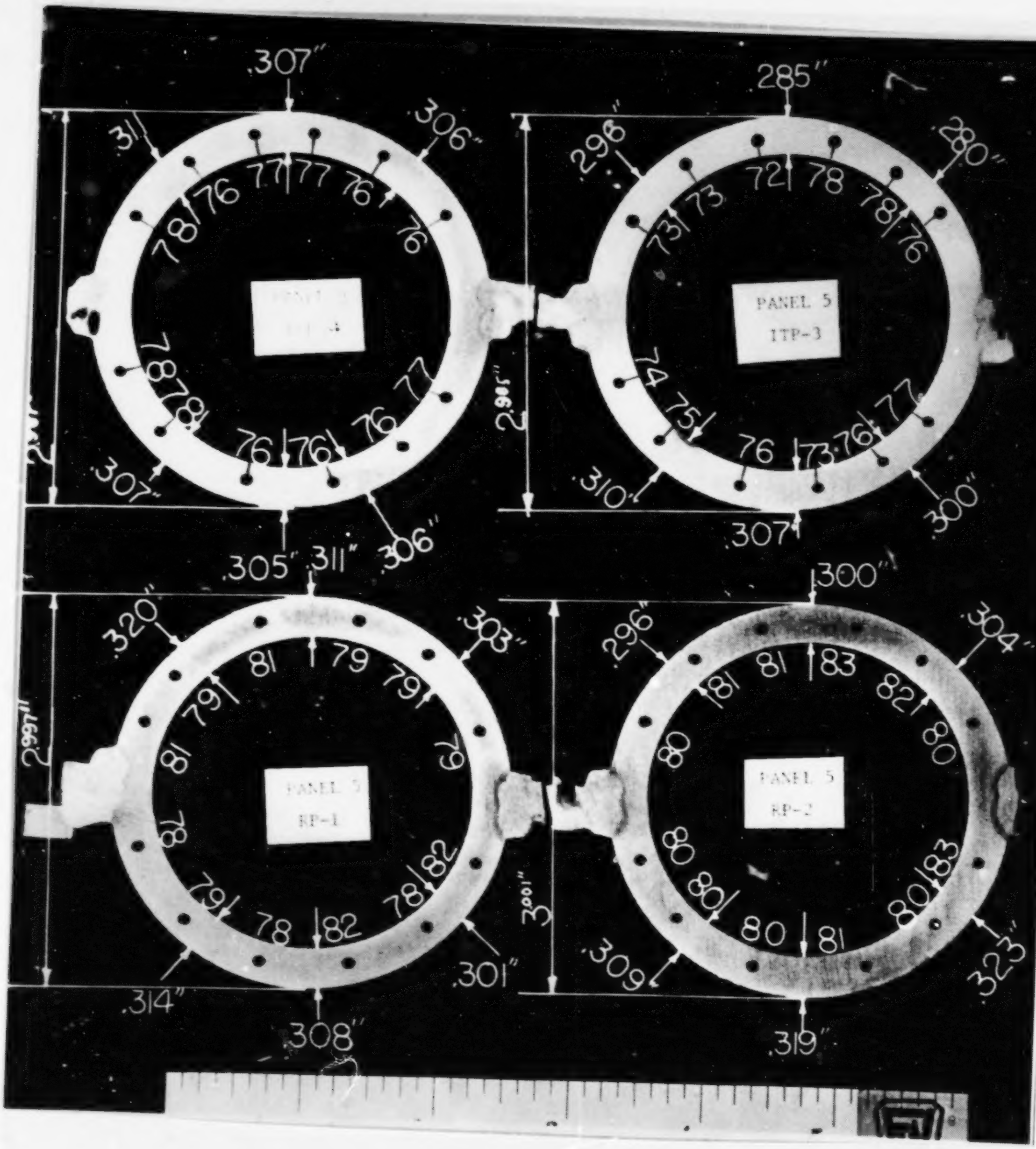

.307"
.311
.306"
77 77
76 76
78 76
2.98"
78 78 78
76 76 76
77
.307"
.305"
.306"
.285"
.296"
.280"
72 78
73 73
78 76
PANEL 5
ITP-3
2.985"
74 75
76 73 76
77
.310"
.307
.300"
.311"
.320"
.303"
81 79
79 79
81 79
PANEL 5
RP-1
2.997"
78
79 78 82
78 82
.314"
.308"
.301"
.300"
.296"
.304"
81 81 83
82 80
80
PANEL 5
RP-2
3.001"
80 80
80 81
80 83
.309"
.319"
.323"

FIGURE 26

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of initial test panel tubes.
BOTTOM: Transverse sections of replacement panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from tubes in Panel No. 5 (Set 2) shown in Figure 16.

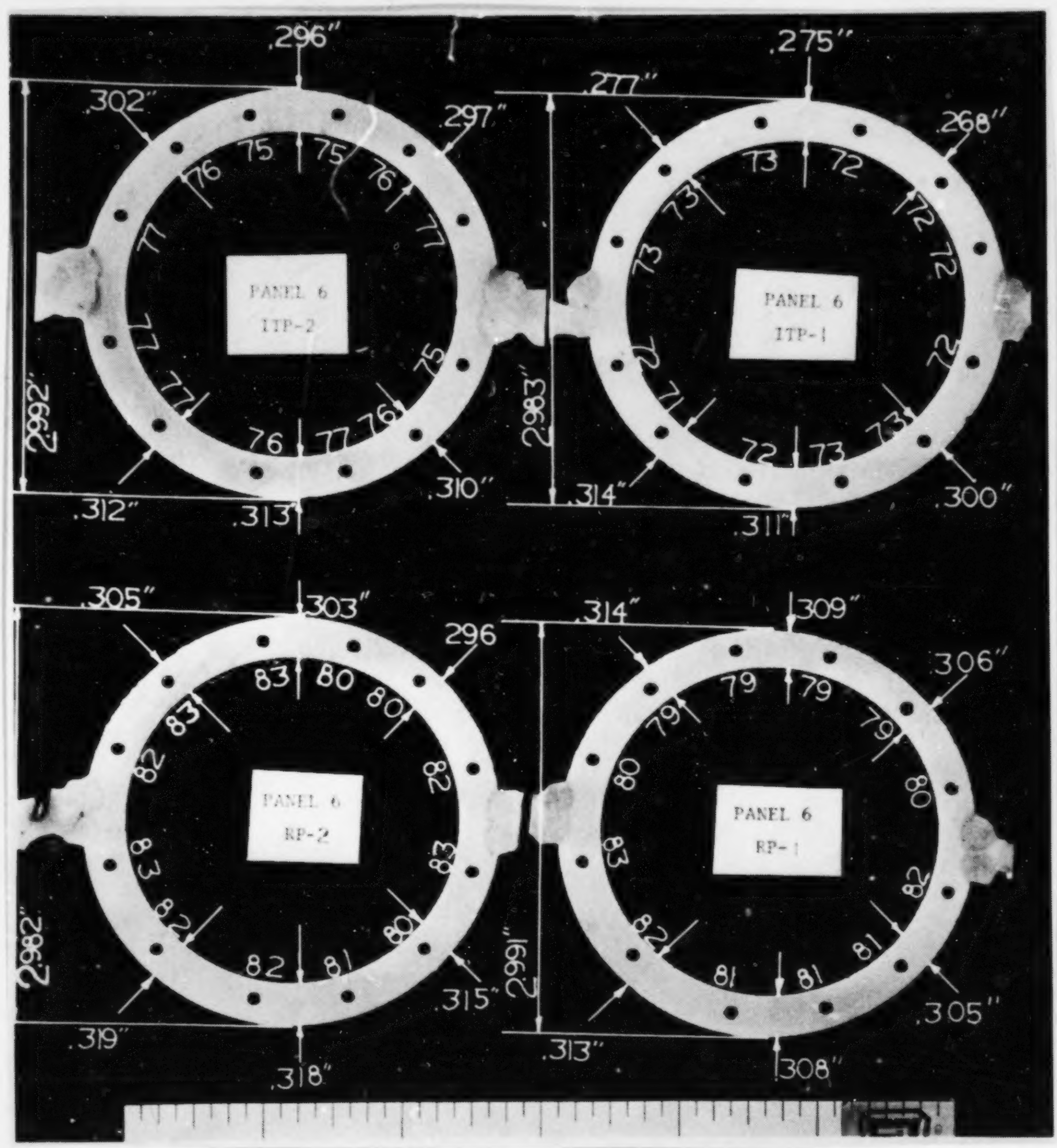

.296"
.275"
.302"
.297"
.277"
.268"
75
75
76
76
77
77
77
77
77
76
76
77
75
73
72
73
72
72
73
72
71
72
72
73
73
PANEL 6
ITP-2
PANEL 6
ITP-1
2.992"
2.983"
.312"
.313"
.310"
.314"
.311"
.300"
.305"
.303"
296
.314"
.309"
.306"
83
80
83
80
82
82
83
83
82
82
81
80
79
79
79
79
80
80
83
82
82
81
81
81
PANEL 6
RP-2
PANEL 6
RP-1
2.982"
2.991"
.319"
.318"
.315"
.313"
.308"
.305"

FIGURE 27

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of initial test panel tubes.
BOTTOM: Transverse sections of replacement panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from tubes in Panel No. 6 (Set 2) shown in Figure 17.

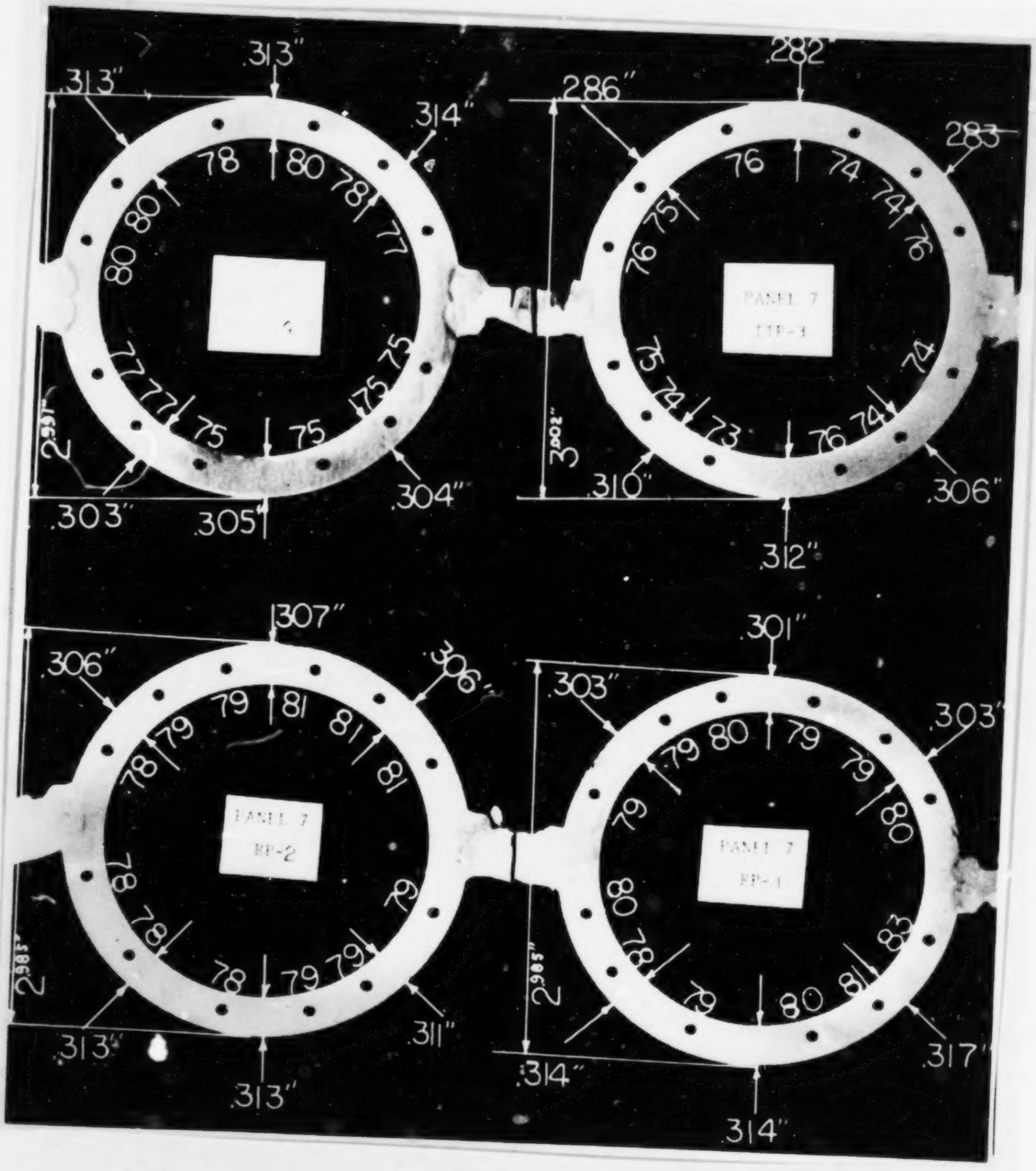
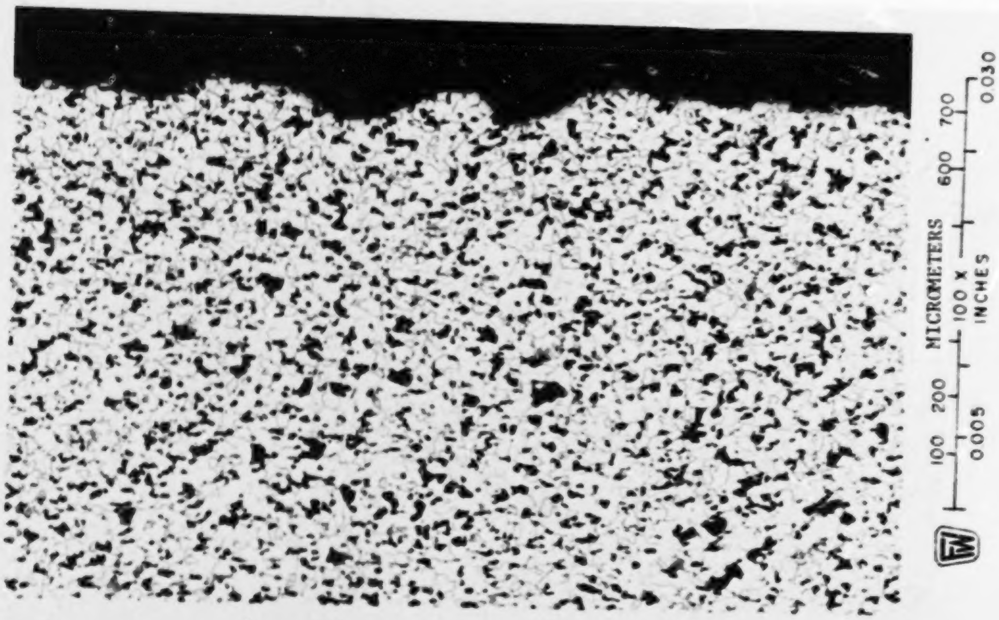

.313"
.313"
.314"
78
80
78
77
80
80
80
77
77
77
75
75
75
75
2.991"
.303"
.305"
.304"
.282"
.286"
.283"
76
74
74
76
75
76
PANEL 7
ITP-3
75
74
73
76
74
74
3.002"
.310"
.306"
.312"
.307"
.306"
.306"
79
81
81
81
79
78
PANEL 7
RP-2
78
78
78
78
79
79
79
2.985"
.313"
.313"
.311"
.301"
.303"
.303"
79
80
79
79
80
79
PANEL 7
RP-1
80
78
79
80
81
83
2.985"
.314"
.314"
.317"

FIGURE 28

PHOTOMACROGRAPH 1X MAGNIFICATION CUT/GROUND

TOP: Transverse sections of initial test panel tubes.
BOTTOM: Transverse sections of replacement panel tubes.

Photomacrograph illustrates the appearances of transverse ring sections removed from tubes in Panel No. 7 (Set 2) shown in Figure 18.


100
200
MICROMETERS
600
700
0.005
100 X
INCHES
0.030

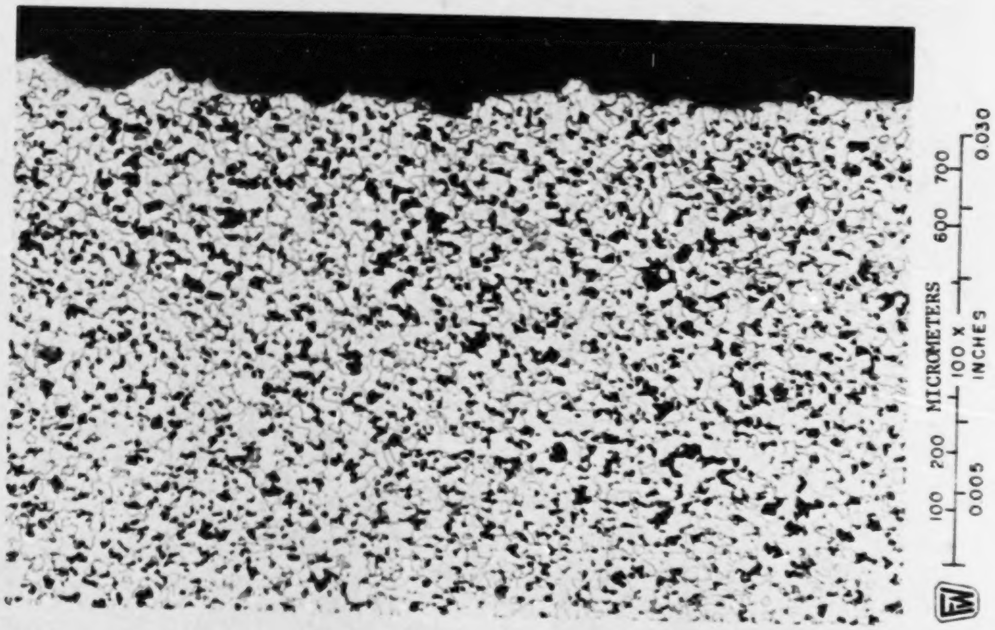

100
200
MICROMETERS
600
700
0.005
100 X
INCHES
0.030

FIGURE 29

PHOTOMICROGRAPHS 100X MAGNIFICATION 2% NITAL ETCH

TOP: Panel No. 6: Original Boiler Tubing: Fireside Surface
BOTTOM: Panel No. 6: Original Boiler Tubing: Cold Side Surface

Photomicrographs illustrate the transverse cross sectional microstructural appearances of specimens removed from the outside surfaces of original boiler tubing which was in service approximately 5 years.

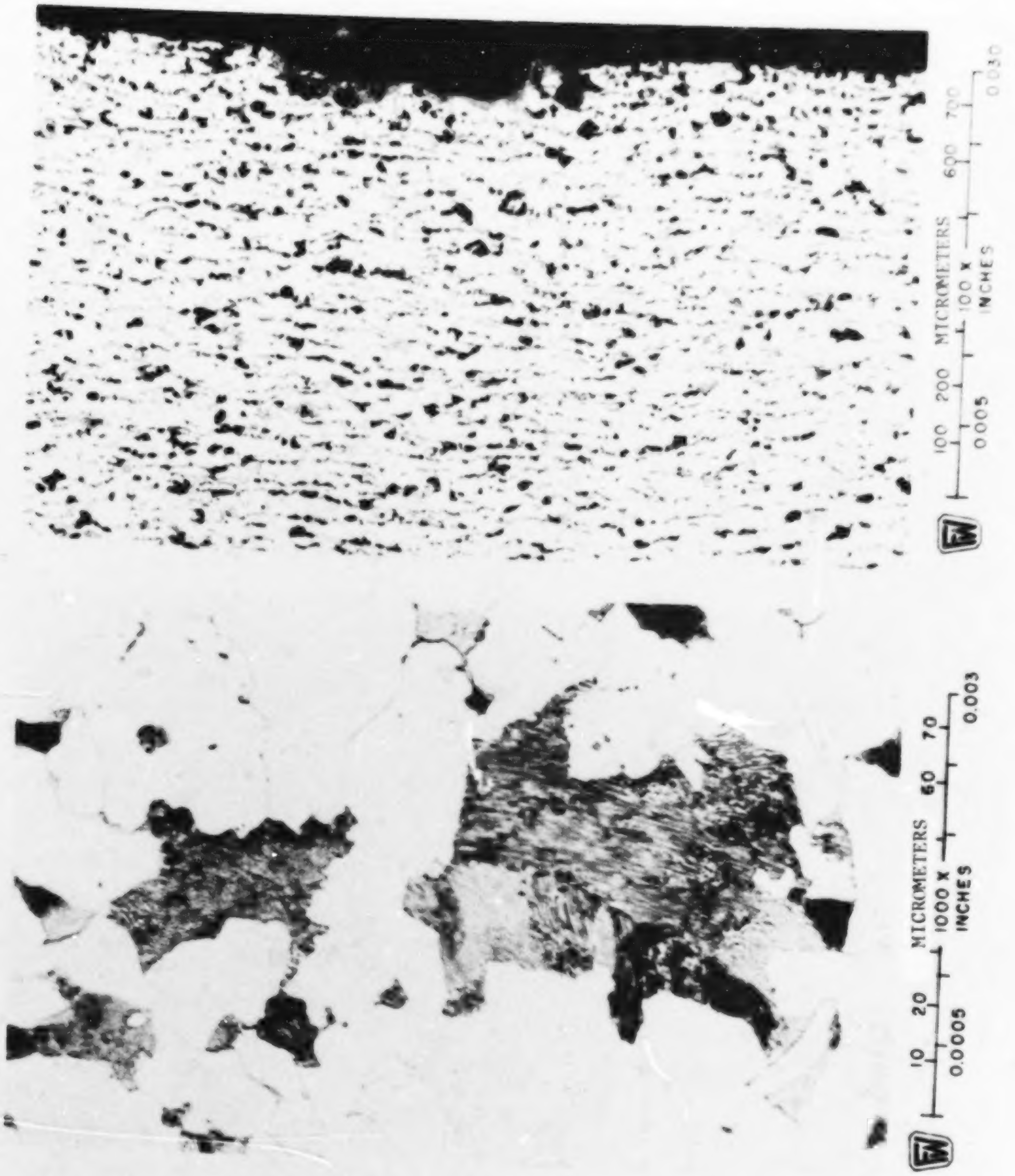

100 200 MICROMETERS 600 700
0.005 100 X INCHES 0.030
10 20 MICROMETERS 60 70
0.0005 1000 X INCHES 0.003

FIGURE 30

PHOTOMICROGRAPHS 100X MAGNIFICATION 2% NITAL ETCH

TOP: Panel No. 6: Original Boiler Tubing: Inside Surfaces
BOTTOM: Panel No. 6: Original Boiler Tubing: High Magnification

Photomicrograph at top illustrates the transverse cross sectional microstructural appearance of specimen removed from the inside surfaces of original boiler tubing section shown in previous Figure 29. Note oxide and corrosion deposits in pitted area. Bottom photomicrograph shows, at higher magnification, the lamellar pearlite/ferrite platelets normally found in as-received normalized carbon steel tubing.

Reproduced from best available copy.

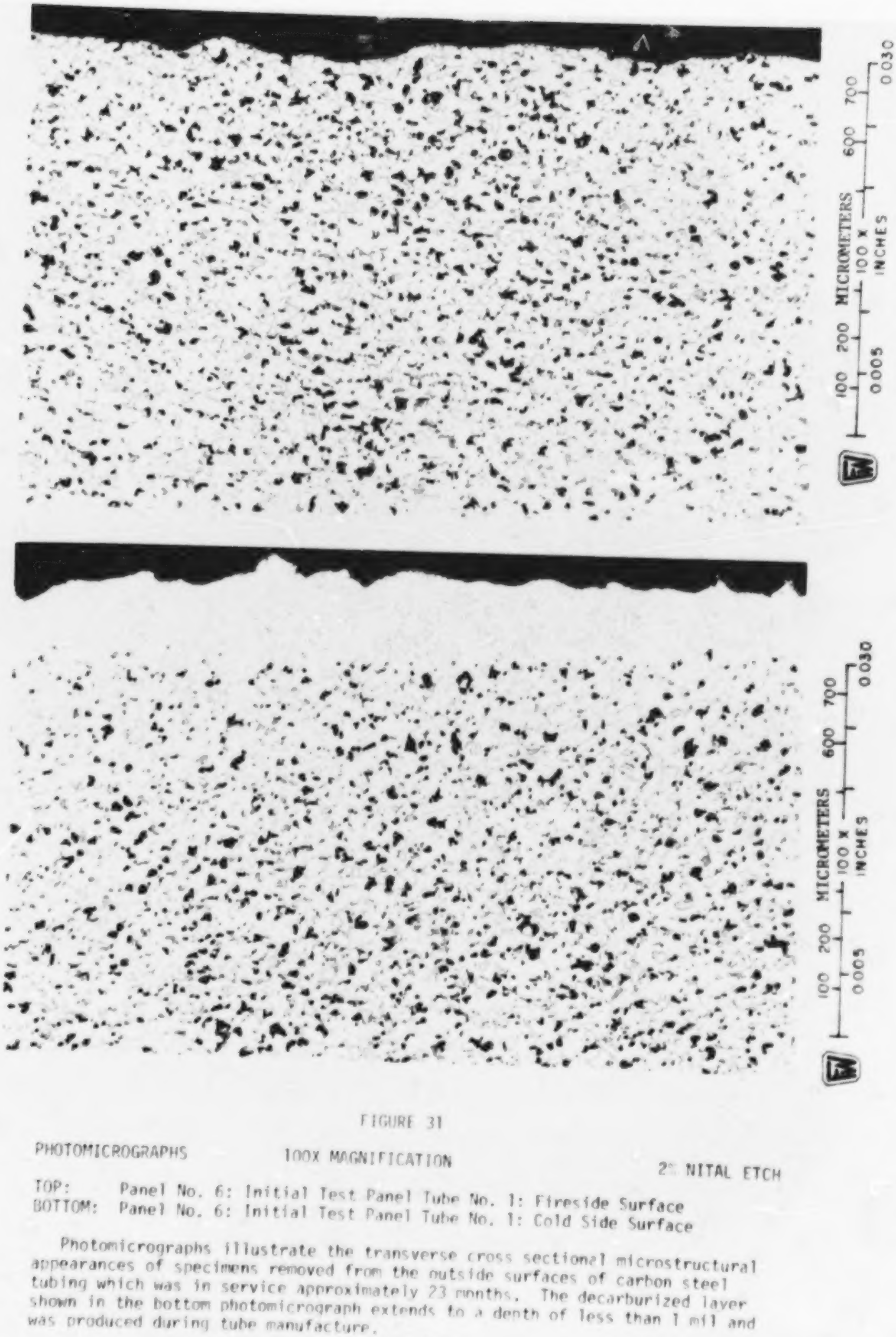

100 200 MICROMETERS 600 700
100 X
0.005 INCHES 0.030
100 200 MICROMETERS 600 700
100 X
0.005 INCHES 0.030

FIGURE 31

PHOTOMICROGRAPHS 100X MAGNIFICATION 2% NITAL ETCH

TOP: Panel No. 6: Initial Test Panel Tube No. 1: Fireside Surface
BOTTOM: Panel No. 6: Initial Test Panel Tube No. 1: Cold Side Surface

Photomicrographs illustrate the transverse cross sectional microstructural appearances of specimens removed from the outside surfaces of carbon steel tubing which was in service approximately 23 months. The decarburized layer shown in the bottom photomicrograph extends to a depth of less than 1 mil and was produced during tube manufacture.

NOT REPRODUCIBLE

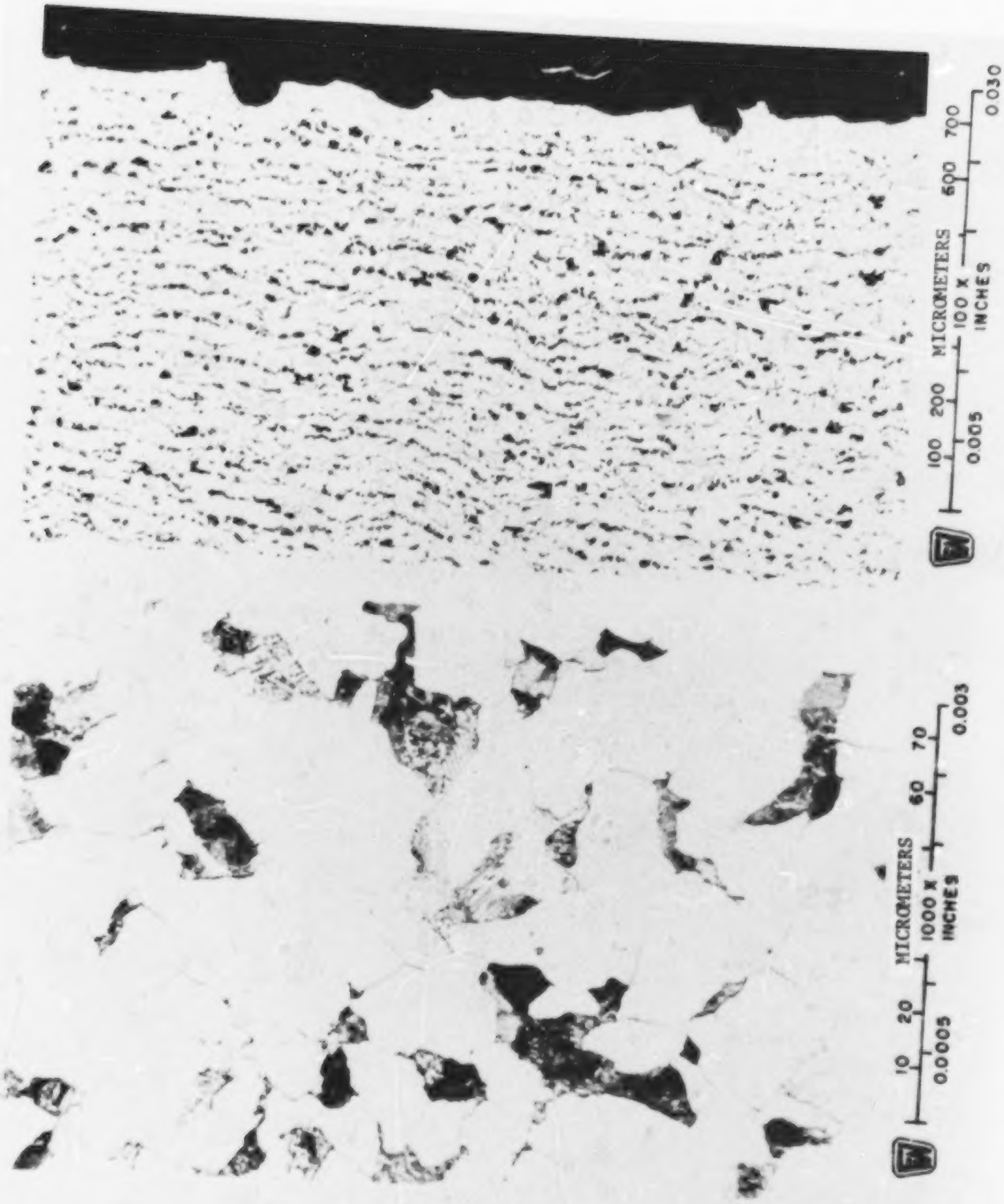

MICROMETERS
100
200
600
700
100 X
INCHES
0.005
0.030
MICROMETERS
10
20
60
70
1000 X
INCHES
0.0005
0.003

FIGURE 32

PHOTOMICROGRAPHS

2% NITAL ETCH

TOP: Panel No.6: Initial Test Panel Tube No.1: Inside Surface: 100X MAGNIFICATION
BOTTOM: Panel No.6: Initial Test Panel Tube No.1: 1000X MAGNIFICATION

Photomicrograph at top illustrates the transverse cross sectional microstructural appearance of specimen removed from the inside surfaces of Initial Test Panel Tube No. 1 shown in previous Figure 31. Some shallow pitting of the inside surfaces is evident. Bottom photomicrograph shows at higher magnification the pearlitic microstructure normally found in as-received normalized carbon steel tubing.

NOT REPRODUCIBLE

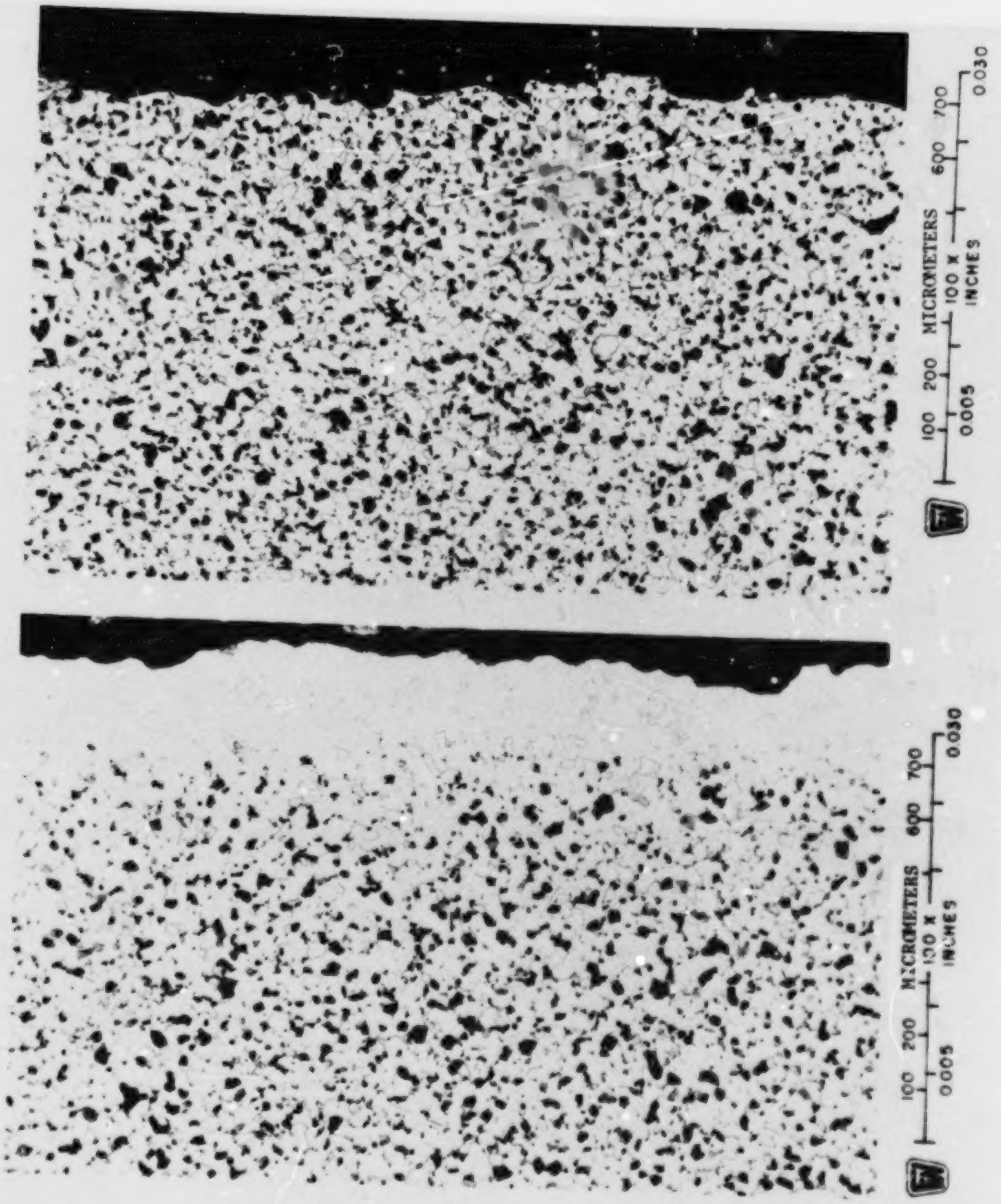

100
200
MICROMETERS
100 X
600
700
0.005
INCHES
0.030
100
200
MICROMETERS
100 X
600
700
0.005
INCHES
0.030

FIGURE 33

PHOTOMICROGRAPHS 100X MAGNIFICATION 2% NITAL ETCH

TOP: Panel No. 6: Initial Test Panel Tube No. 2: Fireside Surface
BOTTOM: Panel No. 6: Initial Test Panel Tube No. 2: Cold Side Surface

Photomicrographs illustrate the transverse cross sectional microstructural appearances of specimens removed from the outside surfaces of 1/2Cr-1/2Mo tubing which was in service approximately 23 months. The decarburized layer shown in the bottom photomicrograph extends to a depth of less than [illegible] mil and was produced during tube manufacture.

NOT REPRODUCIBLE

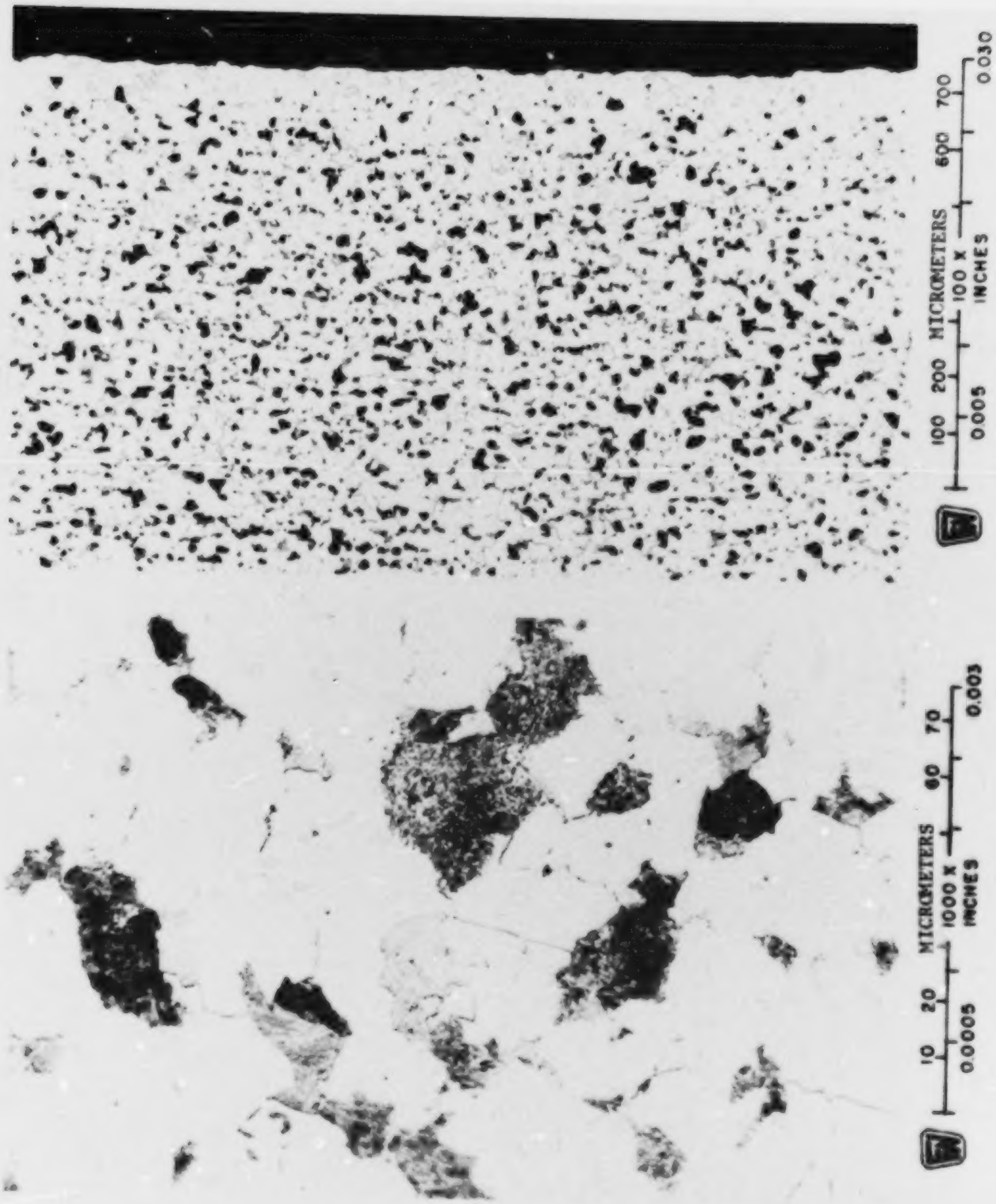

100 X
MICROMETERS
100
200
600
700
INCHES
0.005
0.030
1000 X
MICROMETERS
10
20
60
70
INCHES
0.0005
0.003

FIGURE 34

PHOTOMICROGRAPHS

2% NITAL ETCH

TOP: Panel No.6: Initial Test Panel Tube No.2: Inside Surface: 100X MAGNIFICATION
BOTTOM: Panel No.6: Initial Test Panel Tube No.2: 1000X MAGNIFICATION

Photomicrographs illustrate the cross sectional microstructural appearances of specimen removed from the inside surface of Initial Test Panel Tube No 2 shown in previous Figure 33. Bottom photomicrographs show at higher magnification the alloy rich pearlitic microstructure normally found in as-received normalized 1/2Cr-1/2Mo tubing.

NOT REPRODUCIBLE

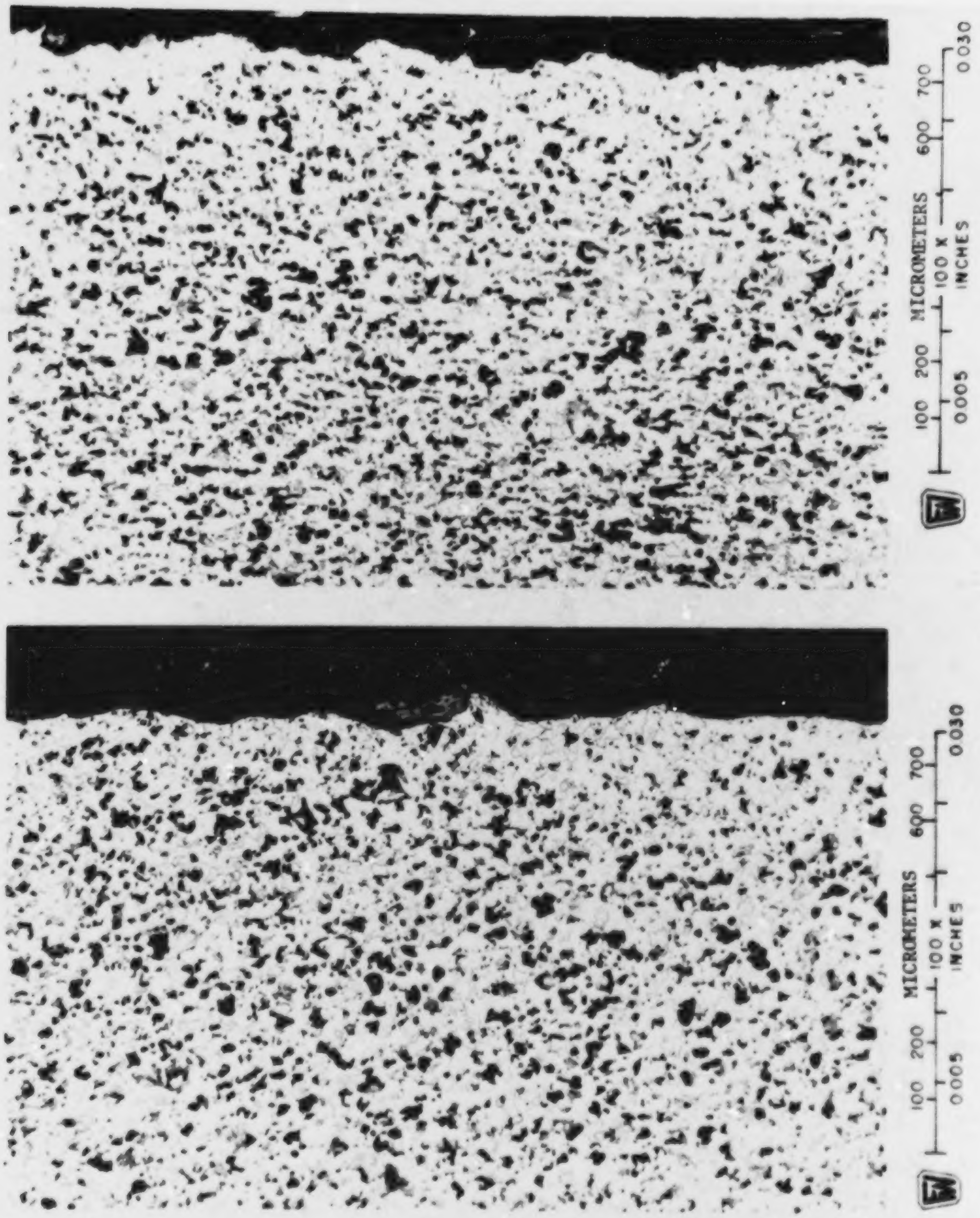


FIGURE 35

PHOTOMICROGRAPHS 100X MAGNIFICATION 2% NITAL ETCH

TOP: Panel No. 6: Replacement Test Panel Tube No. 1: Fireside Surface
BOTTOM: Panel No. 6: Replacement Test Panel Tube No. 1: Cold Side Surface

Photomicrographs illustrate the transverse cross sectional microstructural appearances of specimen removed from the inside surface of Replacement Panel Tube No. 1 which was in service approximately 6 months. Note that tubing was not decarburized during manufacture.

NOT REPRODUCIBLE

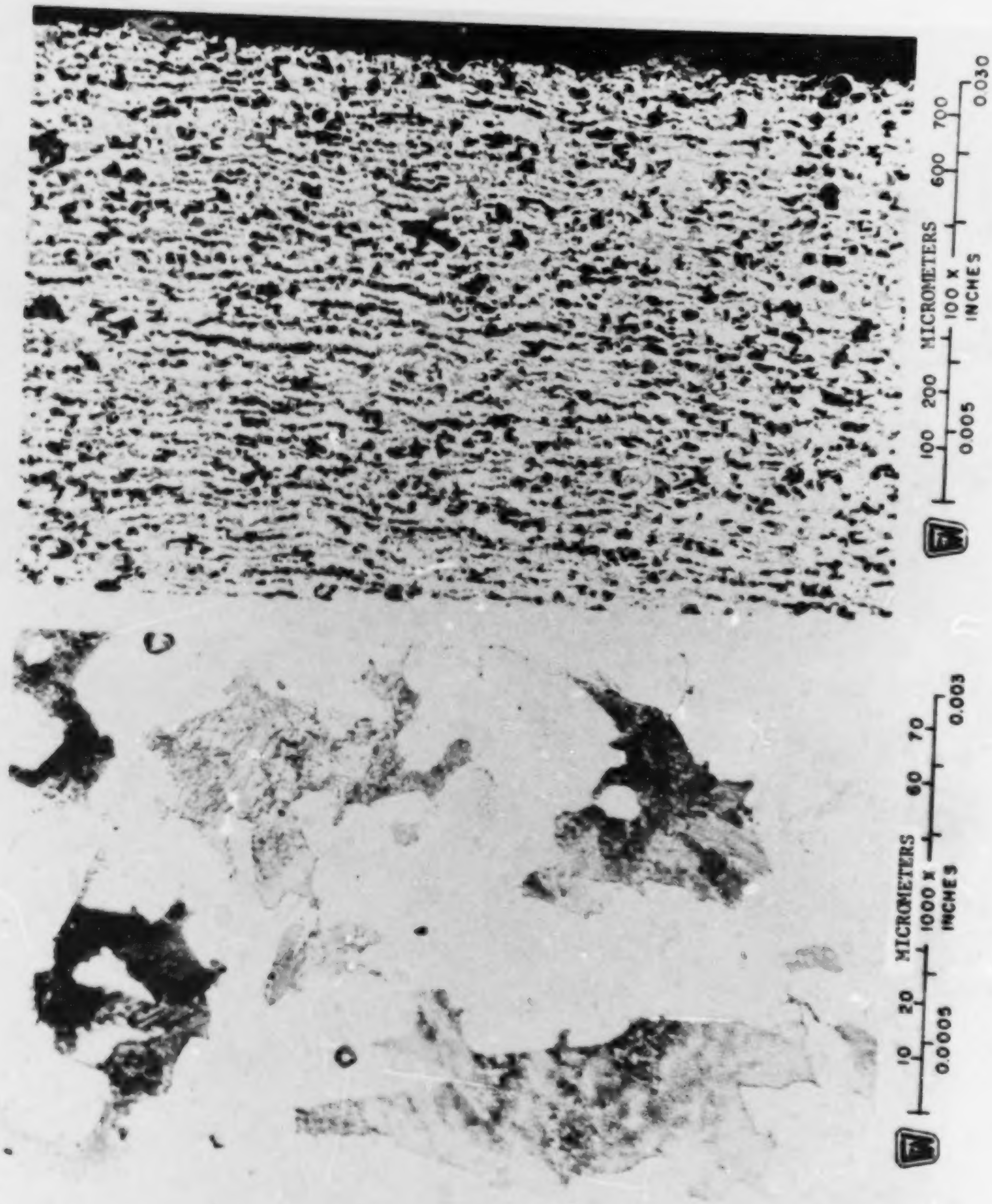

100 200 MICROMETERS 600 700
100 X
0.005 INCHES 0.030
10 20 MICROMETERS 60 70
1000 X
0.0005 INCHES 0.003

FIGURE 36

PHOTOMICROGRAPHS

2% NITAL ETCH

TOP: Panel No.6: Replacement Test Panel Tube No.1: Inside Surface: 100X MAGNIFICATION
BOTTOM: Panel No.6: Replacement Test Panel Tube No.1: 1000X MAGNIFICATION

Photomicrograph at top illustrates the transverse cross sectional microstructural appearances of specimen removed from the inside surfaces of Replacement Test Panel Tube No. 1 which was in service approximately 6 months. Bottom photomicrograph shows at higher magnification the large grain size containing pearlitic constituents normally found in as-received normalized carbon steel tubing.

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